Improving the flexibility, electrical conductivity and light absorption of carboxymethylcellulose and polyvinyl alcohol solutions and thin films by the addition of different concentrations of citric acid.

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Abstract: The aim of this research is to improve certain physical properties of carboxymethylcellulose, polyvinyl alcohol and benefit from this improvement in many areas. CMCHV and PVA solutions were prepared by dissolving them in twice-distilled water, then different concentrations of citric acid (0.0, 40, 57, 66, 72%) were added, also a new solutions for the samples were prepared in the same way then the solutions were poured onto a level glass plate and allowed to dry at room temperature (30ºC), so thin films almost 0.01 mm thick were formed. After that, the ultraviolet absorbance of the solutions, the electrical conductivity of the samples, and the mechanical properties of the thin film samples were measured. From the results, it is clear that with increasing acid concentration, the UV absorbance of all solution samples increased and thus the spectral transmittance through the samples decreased and the solutions became somewhat opaque. The optical density of the solution of each of CMCHV and PVA increased. The optical density increase for solution CMCHV was greater than that for solution PVA at a certain concentration of acid, also the optical density for solution PVA was greater than that for solution CMCHV at another concentration. as well as the conductivity of all samples (solutions and thin films), increases with increasing citric acid concentration, so that the conductivity of CMCHV increases more than the conductivity of PVA. For the CMCHV solutions, two peaks appeared at wavelengths (198nm) and (223nm) in the absorption curve of the ultraviolet spectrum, and three peaks at wavelengths (198 nm), (203 nm) and (224) appeared for the PVA solutions. The conductivity of CMCHV thin films increases more than that of PVA thin films with increasing temperature. For elastic properties of samples, the citric acid concentrations reduce the elasticity of CMCHV thin films and increase the elasticity PVA of thin films. These results can be used in many fields, such as the oil field, medicine field, or scientific research.

Keywords: Carboxymethyl cellulose, Polyvinylalcohol, Conductivity, Elastic properties, UV-VIS absorption, thin film.

Introduction:

Ultraviolet spectroscopy is a type of absorption spectroscopy in which the molecule absorbs light from the UV region from 10 nm to 400 nm, resulting in the excitation of electrons from ground state to a higher energy state [1, 2]. Using the amount of light and wavelength absorbed, valuable information can be obtained, such as the purity of a substance. Furthermore, the amount of light absorbed is related to the amount of substance and quantitative analysis can be performed using optical spectroscopy. [3]. Carboxymethylcellulose is a representative cellulose derivative with carboxymethyl groups attached to some of the hydroxyl groups of the cellulose backbone. It can be easily synthesized by alkaline reaction of cellulose with chloroacetic acid and has been widely used as a thickening and stabilizing agent [4]. CMC comes in the form of a white or slightly yellow flocculating fiber powder, or white powder. It is odorless, tasteless, non-toxic, and is soluble in cold or hot water to form a certain degree of transparent solution adhesion. CMC is a natural organic polymer, the most abundant, biocompatible and biodegradable bio macromolecule. [5]. Polyvinyl alcohol has several interesting physical properties that are very useful in materials science and engineering applications. Polyvinyl alcohol as a water-soluble semicrystalline material exhibits certain physical properties resulting from amorphous crystalline interfacial effects. Polyvinyl alcohol is a polymer that has a carbon backbone with hydroxyl groups attached to the methane carbons. OH- groups can be a source of hydrogen bonds and therefore contribute to the formation of polymers [6]. Citric acid is one of the organic acids that can be used to produce high-value products, including foods and beverages, detergents, medicines, cosmetics and toiletries, among others. As citric acid is a high-value product, it has recently attracted much attention in terms of biological synthesis [7]. Citric acid is a natural source of organic acid found in all citrus fruits. The name is derived from the Latin word citrus and is synthesized by biochemical reaction in a living cell. The pure form of citric acid is easily soluble in water, colorless and solid at room temperature [8]. The mechanical properties of polymers are one of the characteristics that distinguish them from small molecules. The mechanical properties of a polymer involve its behaviour under tension. These properties tell a polymer scientist or engineer what he needs to know when he thinks about how a polymer can be used [9]. Generally, if filler is added to the polymer, the mechanical properties of the composite are improved, and the degree of improvement in mechanical properties depends on several factors [10]. Conductivity is a measure of the quality of a solution to conducts electricity. To carry a current, a solution must contain charged particles or ions. Most conductivity measurements are performed in aqueous solutions and the ions responsible for conductivity come from electrolytes dissolved in water [11]. The Siemens (S) is the International Standard (SI) unit of electrical conductance. Siemens is also used, when multiplied by imaginary numbers, to indicate susceptibility in alternating current and radio frequency applications [12].

2. Materials and Measurements:

2.1 Materials and Samples preparation :

2.1.1 Materials:

Carboxymethyl cellulose high viscosity (CMC HV) was obtained from National Oil Corporation Jowfe Oil Technology/ Ganfouda/ Benghazi/ Libya, Polyvinylalcohol (PVA) (99+40 hydrolyzed, Mw 85000 g mol^{-1}), was supplied by Sigma-Aldrich GMBH, and citric acid was prepared in the laboratory.

2.1.2 Samples preparation

2.1.2.1 Solutions of Samples

The CMCHV solutions were prepared by dissolving the CMC HV in twice-distilled water, then added to different concentrations of citric acid (0.0, 40, 57, 66, 72 %), while stirring at room temperature (30^{o}C), and PVA solutions were prepared in the same way as CMCHV solution.

2.1.2.2 Thin films of Samples

New solutions for the samples were prepared in the same way as the solutions in paragraph (2.1.2.1), then the solutions were poured onto a level glass plate and allowed to dry at room temperature (30^{o}C). Thin films almost 0.01 mm thick were formed.

2.1.2.3 Preparation of citric acid

Put the lemon juice in a graduated container, then add the same amount of water and soda, adding it slowly. The mixture is filtered, a calcium chloride solution is added, a precipitate of calcium citrate forms. Boil for two minutes and filter. Sulfuric acid is slowly added and calcium sulfide precipitates to form citric acid. Which is filtered with filter paper and the acid is concentrated over low heat to form crystals and dried in the oven.

2.2 The theory

2.2.1 Absorption and transmission of UV- VIS Spectra

By knowing the amount of absorption(a), the transmission (T) is calculated in using equation (1), and from the transmission percentage, the optical density (OD) is calculated by equation (2) [13, 14] .

$$a = -\log \frac{1}{T} \qquad (1)$$

$$OD = \log \frac{100}{T\%} \qquad (2)$$

2.2.2 The conductivity

From the conductivity (σ), the resistivity (ρ) can be calculated from the equation (3).
[15]

$$\rho = \frac{1}{\sigma} = \frac{R\,A}{L} \qquad (3)$$

Using equation (4), the value of conductance (G) is calculated, where (A) is the surface area, R is the resistance and (L) is the depth of conductivity measuring point within the solution [15].

$$G = \sigma\left(\frac{A}{L}\right) \qquad (4)$$

The relationship between the electric current density (J) and the electric field (E) represented by Ohm's law is known as equation (6) [16].

$$J = \frac{I}{A} \qquad (5)$$

And:

$$J = \sigma E \qquad (6)$$

Where I is the current intensity, and L is the thickness of the sample [17].

2.2.3 Elastic properties

If force (F) applied on the thin films and the cross section (A) of the thin films then the stress (S) and strain (Є) represented in equation (8) and equation (9) respectively [18, 19].

$$S = \frac{F}{A} \qquad (8)$$

$$\epsilon = \frac{(L - L_0)}{L_0} \qquad \mathbf{(9)}$$

where the original length (L_o) of the thin film was measured, as well as the lengths (L) of the samples after changing them by applying forces [18]. But *Young's modulus* (Y) can be calculated using equation (1) [18,20].

$$Y = \frac{S}{\epsilon} \qquad (10)$$

2.3 Experiments and Calculations

Some measurements were carried out in the laboratory of the Department of Chemistry, Faculty of Science, University of Benghazi.

2.3.1 Absorption and transmission of UV- VIS Spectra

The ultraviolet absorption spectrum of the solutions was measured using a spectrometer (Product: Libra S 50, Version: 5502 V 1.0.0, Serial number: 113342), which is shown in figure (1), Then, the transmission and optical density values were calculated using equations (1) and (2), respectively.

Fig.1 The ultraviolet absorption spectrometer.

2.3.2 The conductivity

2.3.2.1 Conductivity of solutions

The conductivity of the sample solutions was measured using a electrical conductivity meter as shown in figure (2).

Fig. 2 Electrical conductivity meter

2.3.2.2 Conductivity of thin films

The direct current intensity I was measured for all samples by changing the potential difference V at different temperatures T, starting from room temperature (298.15K) to temperature (348.15K) with a change of 10 degrees. The resistance was then calculated for each sample at all temperatures, while the conductivity was the reciprocal of the resistances, and from there the current density was calculated using equation (6) and the electric field was calculated from the equation (7). Using electrical conductivity and temperature, the activation energy is calculated by the equation (8).

2.3.3 Elastic properties

By fixing the thin film of the sample in the tensioning device and changing the loads that cause the tension, from which the force that causes the expansion of the sample was calculated, as well as the cross section of the sample, its original length and its length was also measured after stretching. Therefore, it is possible to calculate the stress and strain using equations (9) and (10), respectively. Using the stress and strain values, Young's modulus was calculated by using equation (11).

3. Results and discussion

3.2.1 Absorption and transmission of UV- VIS Spectra

Figure (3) shows wavelength vs absorption of uv-vis spectrum in Solutions of CMCHV Samples. It is clear from the figure that as the acid concentration increases, the absorption of the ultraviolet spectrum by the CMCHV increases and there are two absorption peaks at wavelengths (198 nm) and (223 nm).

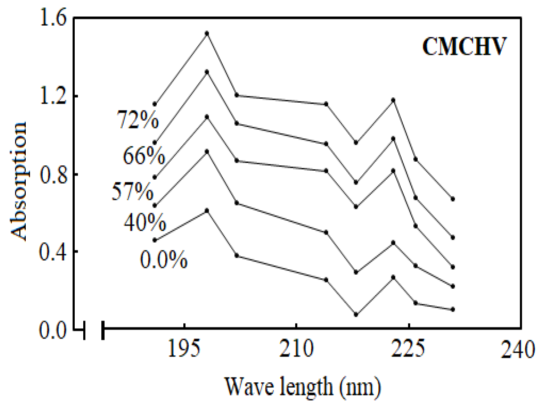

Fig. 3 Wavelength vs absorption of uv-vis spectrum in Solutions of CMCHV Samples.

Transmission values of the ultraviolet spectrum by the CMCHV were calculated from equation (1) and plotted versus wavelengths in figure (4). The shape of the curves in Figure was similar to the curves in figure (3) for absorption, except that the transmission values in figure (4) are negative.

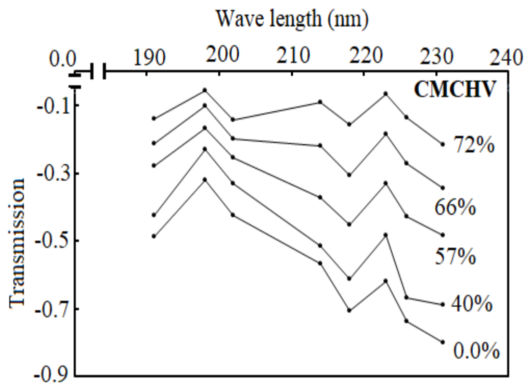

Fig. 4 Wavelength vs transmission of uv-vis spectrum in Solutions of CMCHV Samples.

The absorption of the ultraviolet spectrum by PVA increases as the acid concentration increases, and there are three absorption peaks at the wavelengths (198 nm), (203 nm) and (224 nm), as shown in figure (5).

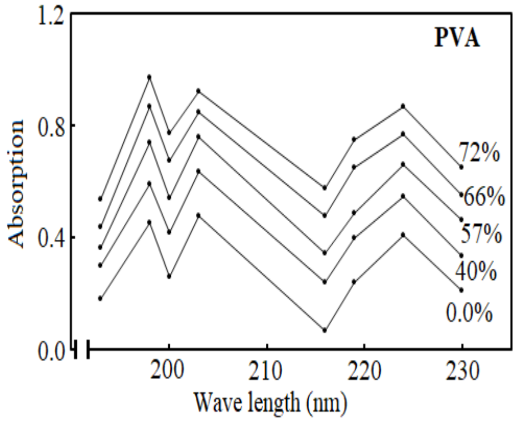

Fig. 5 Wavelength vs absorption of uv-vis spectrum in Solutions of PVA Samples.

Using equation (1), the transmission values of the ultraviolet spectrum by PVA were calculated, then plotted against wavelengths in figure (6). The shape of the curves in figure (6) was similar to the curves in figure (5) for absorption, except that the transmission values in figure (6) are negative.

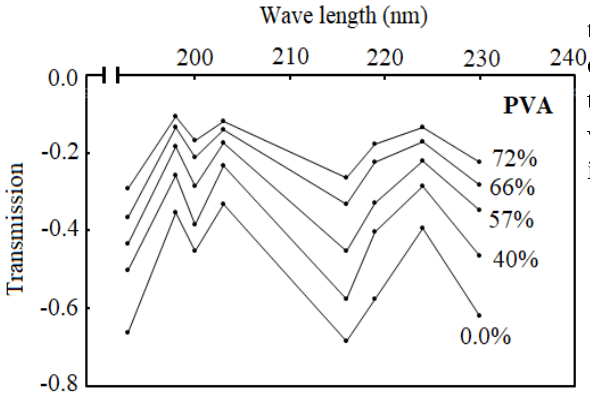

Fig. 6 Wavelength vs transmission of uv-vis spectrum in Solutions of PVA Samples.

Table (1) shows the change in optical density with change in the concentration of citric acid in the samples.

Table.1 Optical density of samples according to citric acid concentration

concentrations of citric acid	PVA OD	CMCHV OD
0.0%	0.193213	0.169724
40%	0.324165	0.300101
57%	0.445731	0.490977
66%	0.582081	0.688187
72%	0.703541	0.98634

3.2.2 The conductivity

3.2.2.1 Conductivity of solutions

When studying figure (7), it is observed that the conductivity of all solutions increases with increasing concentrations of citric acid, but the conductivity of CMCHV increases more than the conductivity of PVA.

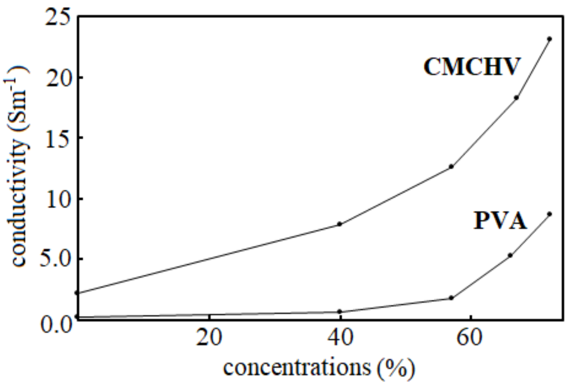

Fig. 7 The conductivity of solutions vs the concentration of citric acid.

The change in the resistivity values of the solutions and their conductance, which were calculated by equation(3) and equation(4), respectively, appears in the values recorded in table (2), and the resistivity values indicate that it decreases with the increase in acid concentration, which confirms the increase in the conductivity of the solutions.

Table. 2 the resistivity values of the solutions and their conductance.

C (%)	PVA		CMCHV	
	ρ(cm/S)	G(S)	ρ(cm/S)	G(S)
0	4.761905	5.275200	0.467290	53.75680
40	1.589825	15.80048	0.127877	196.4384
57	0.558659	44.96480	0.079554	315.7584
66	0.190840	131.6288	0.054885	457.6864
72	0.115207	218.0416	0.043178	581.7792

3.2.2.2 Conductivity of thin films

From figure (8), it is clear that the current density passing through the thin films of CMCHV increases with increasing citric acid concentration as well as increasing temperature, where this figure represents a direct relationship between the intensity of the electric field and the current density. This result is supported by the figure (9), which represents the relationship between the square root of the electric field intensity and the logarithm of the current density.

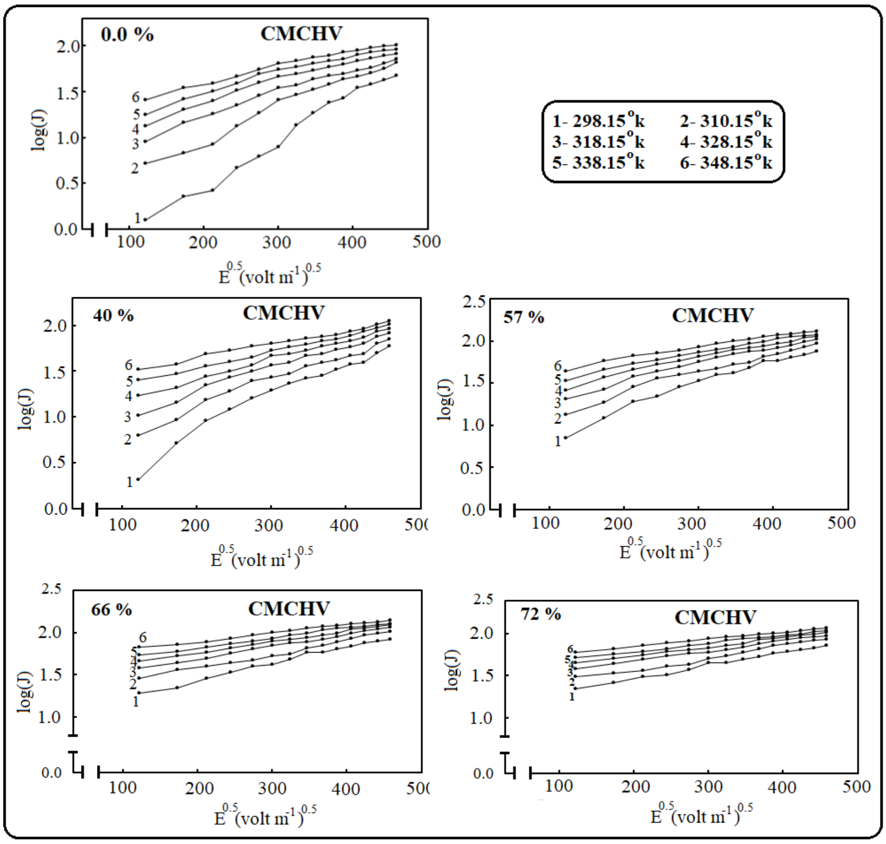

Fig. 8 The current density of CMCHV thin film vs the electric field.

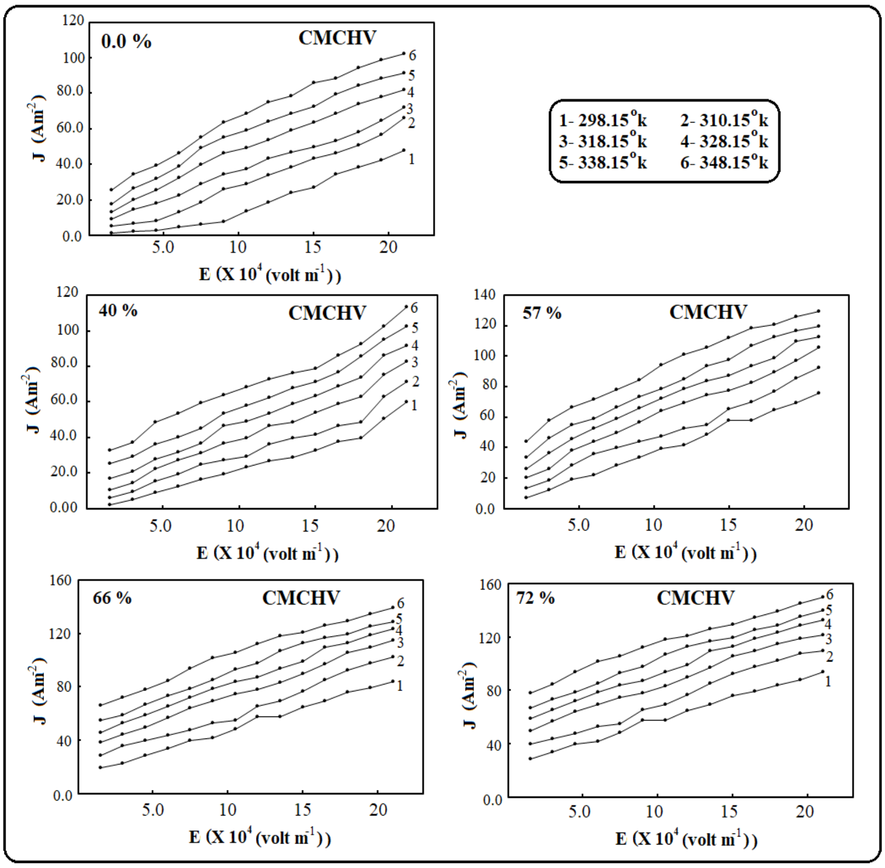

Fig. 9 The logarithm of current density of CMCHV thin film vs the square root of electric field

The inverse relationship between the reciprocal of temperature and the logarithm of the conductivity of CMCHV thin films presented in figure(10) indicates that increasing the temperature of the samples reduces their electrical resistance,

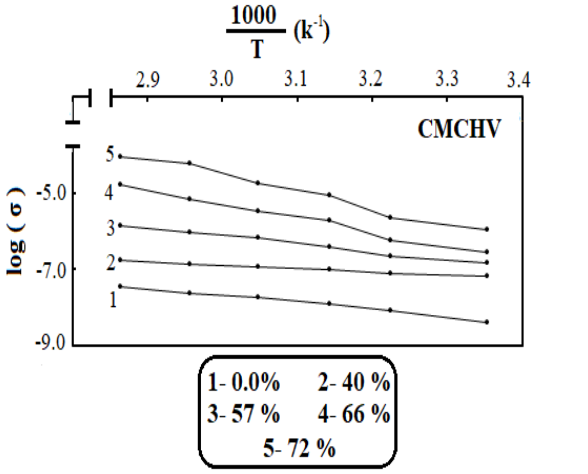

Fig. 10 The logarithm of conductivity of CMCHV thin film vs the inverse of temperature.

Figure (11) shows similar measurements but for PVA samples/solutions. It shows that the current density passing through the thin films of PVA increases with increasing citric acid concentration as well as increasing temperature, where this figure represents a direct relationship between the intensity of the electric field and the current density. This result is supported by the figure (12), which represents the relationship between the square root of the electric field intensity and the logarithm of the current density.

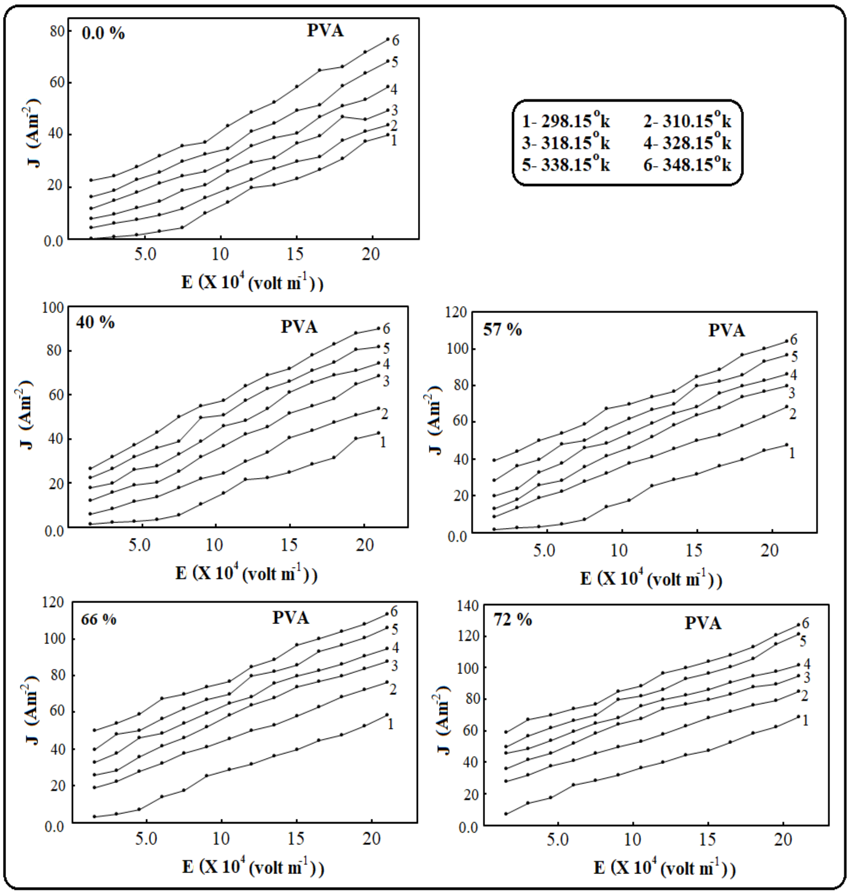

Fig. 11 The current density of PVA thin film vs the electric field.

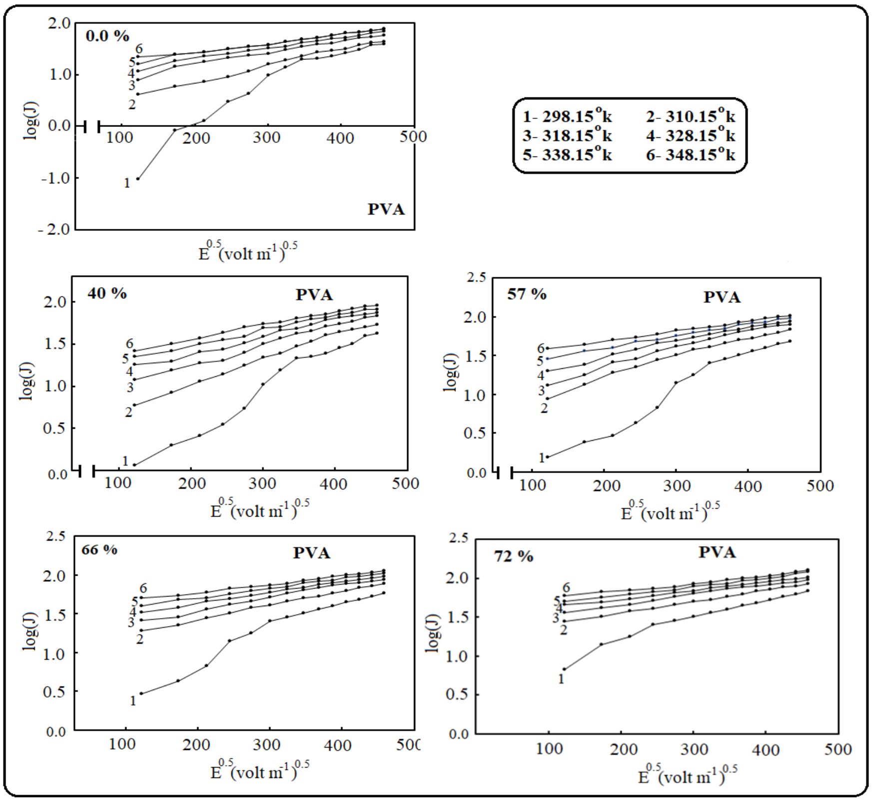

Fig. 12 The logarithm of current density of PVA thin film vs the square root of electric field.

The inverse relationship between the reciprocal of temperature and the logarithm of the conductivity of PVA thin films in figure(13) indicates that increasing the temperature of the samples reduces their electrical resistance.

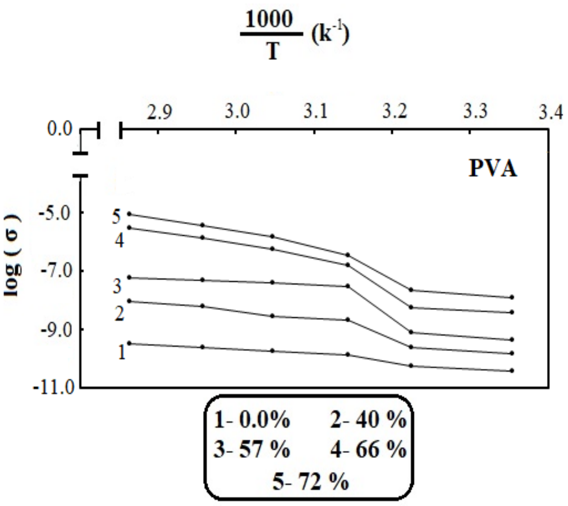

Fig.13 The logarithm of conductivity of PVA thin films vs the inverse of temperature.

It is obvious from the above results that the conductivity of CMCHV thin films increases more than the conductivity of PVA thin films as citric acid concentrations and temperature increase.

3.2.3 Elastic properties

The stress-strain curve presented in figure (14) shows that the increased concentrations of citric acid in the CMCHV thin films lead to decreased flexibility and stress tolerance, while increasing the concentration of citric acid in PVA thin films, their flexibility and stress tolerance increases, as shown in the figure (15).

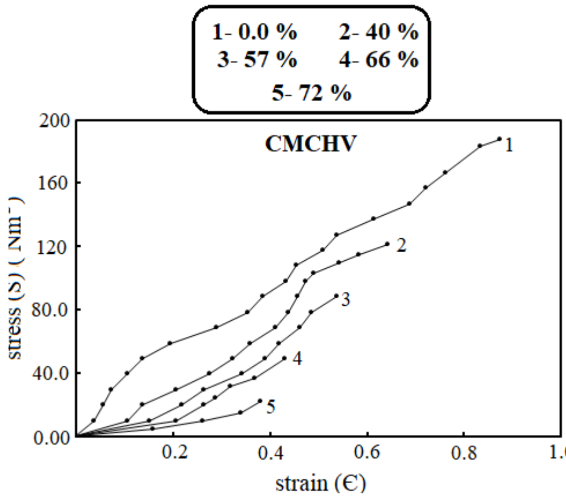

Fig.14 Stress-strain curve for CMCHV thin films.

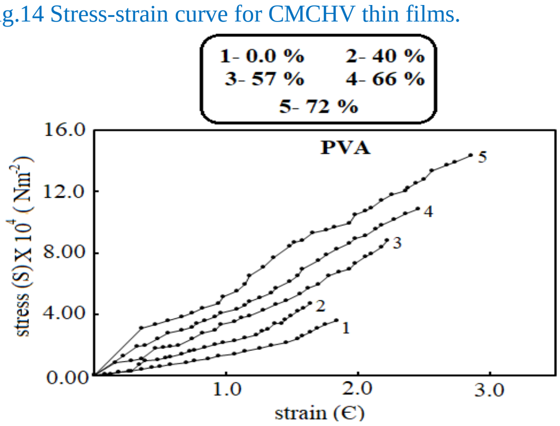

Fig.15 Stress-strain curve for PVA thin films

Figure (16) represents the relationship between the concentrations of citric acid in the thin films and their Young coefficients. Figure (16a) shows an inverse proportion between concentrations and Young's coefficient of CMCHV thin films CMCHV thin films, while figure (16b) shows a direct proportion between concentrations and Young's coefficient of PVA thin films. That is, citric acid concentrations reduce the elasticity of CMCHV thin films and increase the elasticity PVA of thin films.

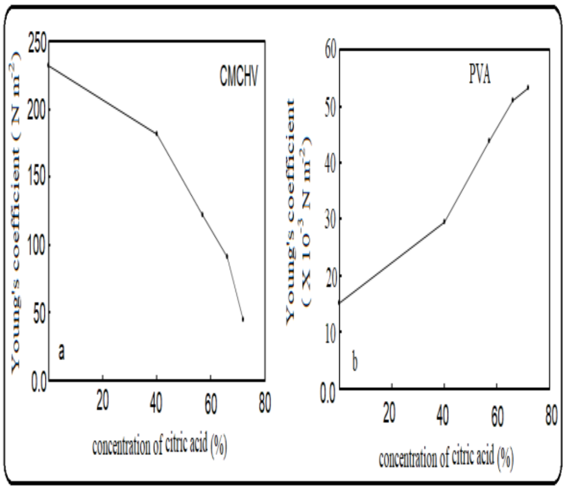

Fig. 16 Young's modulus vs concentrations of citric acid.
(a)Young's modulus of CMCHV thin films, and
(b) Young's modulus of PVA thin films.

Conclusion:

In conclusion, the results show that as the acid concentration increases, the UV absorption of all solution samples, as well as the conductivity of all samples (solutions and thin films), increases with increasing citric acid concentration, so that the conductivity of CMCHV increases more than the conductivity of PVA. The conductivity of CMCHV thin films increases more than that of PVA thin films with increasing temperature. For elastic properties of samples, the citric acid concentrations reduce the elasticity of CMCHV thin films ~~and~~ while increase the elasticity PVA of thin films. These results can be used in many fields, such as the oil field (Such as use to protect oil wells), medicine field(Possible in the pharmaceutical industry), or scientific research (In improving other polymers by adding citric acid).

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