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## Fabrication and Characterization of High-Performance Crosslinked PVA/ PMDA Doped with H<sub>2</sub>SO<sub>4</sub>

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### Abstract

In the present study, pure Poly(vinyl alcohol) (PVA) and pyromellitic dianhydride (PMDA) cross linked PVA with (0,5,10,15 and 20)wt.% and doped with different molarity (5,9)M of sulfuric acid (H<sub>2</sub>SO<sub>4</sub>) were prepared by the solution casting method and were characterized as a function of frequency in the range (1-100) KHz.

The FT-IR results showed that the strong broad band observed at 3738.05 and 3857.63 cm<sup>-1</sup> may be assigned to O-H stretching due to the strong hydrogen bond of intramolecular and intermolecular type in PVA film. When PVA is doped with 5M and 9M H<sub>2</sub>SO<sub>4</sub>, a new peak was noticed at 813 cm<sup>-1</sup>, this peak may be due to the formation of hydrogen bond between the carbonyl (C=O) group of PVA and the H<sup>+</sup> ion from the acid.

As the PMDA concentration increases, the peak intensity of the O-H band 3738.05 cm<sup>-1</sup> gradually decreases due to the reaction of more -OH groups of the PVA molecules with the -COOH group. Hence, it is difficult for the crosslinked PVA polymer chains to pack and form crystal regions, so the crosslinked PVA polymer chains become more flexible.

The a.c. conductivity increases with the increase of frequency. FTIR spectra specified that the chemical reaction did occur between the PVA and the acid, therefore hydrogen ion (H<sup>+</sup>) can easily be separated from the carbonyl group and become free to move which explains proton conductivity of PVA.

The increase of PMDA concentration has increased free volume and ionic mobility in the film with increasing cross-linkages.

Dielectric constant decreases with increasing H<sub>2</sub>SO<sub>4</sub> molarity for every frequency.

**Keywords:** Solid polymer electrolyte, PVA, pyromellitic dianhydrides, ionic conductivity.

### تصنيع وتوصيف PVA / PMDA عالية الأداء المتشابكة المطعمة بواسطة H<sub>2</sub>SO<sub>4</sub>

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#### الخلاصة

في هذه الدراسة، تم تحضير بولي (فينيل الكحول) (PVA) النقي وروابطه المتشابكة بطريقة صب المحلول وتم توصيفها كدالة للتردد في النطاق (1-100) كيلو هرتز، وتركيز ديانهيدريد البيرومليتيك (PMDA) (0,5,10,15) ومع مولارية مختلفة من حامض الكبريتيك (5 و9) H<sub>2</sub>SO<sub>4</sub>.

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أظهرت نتائج FT-IR أن النطاق العريض القوي الذي لوحظ عند 3738.05 و 3857.63 سم<sup>-1</sup> يمكن ملاحظته في التمدد الحاصل للأصرة O-H بسبب الرابطة الهيدروجينية القوية ذات النوع داخل الجزيئي وبين الجزيئي في غشاء PVA. عندما يتم تطعيم PVA بمقدار 5 مولاري و 9 مولاري من H<sub>2</sub>SO<sub>4</sub> ، لوحظت ذروة جديدة عند 813 سم<sup>-1</sup> ، قد تكون هذه الذروة ناتجة عن تكوين رابطة هيدروجينية بين مجموعة الكربونيل (C = O) من PVA و أيون H<sup>+</sup> من الحامض. يمكننا أن نرى القيم الرئيسية تصبح قوية وأضيق مقارنةً بـ PVA النقي. مع زيادة تركيز PMDA ، تنخفض شدة الذروة لنطاق O - H 3738.05 سم<sup>-1</sup> تدريجيًا بسبب تفاعل مجموعات OH- من جزيئات PVA مع مجموعة COOH-. وبالتالي ، من الصعب على سلاسل بوليمر PVA المتشابهة أن تشكل مناطق بلورية وبذلك تصبح سلاسل بوليمر PVA المتشابهة أكثر مرونة. تزداد موصلية التيار المتناوب مع زيادة التردد. حددت أطراف FTIR أن التفاعل الكيميائي حدث بين PVA و الحامض ، لذلك يمكن فصل أيون الهيدروجين (H<sup>+</sup>) بسهولة عن مجموعة الكربونيل وبالتالي يصبح حر الحركة وهذا يوضح موصلية البروتون لـ PVA. أدت الزيادة في تركيز PMDA إلى زيادة طول سلسلة البوليمر لأغشية PVA التي زادت من الحجم الحر والتنقل الأيوني في الغشاء مع زيادة الروابط المتشابهة. ينخفض ثابت العزل الكهربائي مع زيادة مولارية H<sub>2</sub>SO<sub>4</sub> لكل تردد.

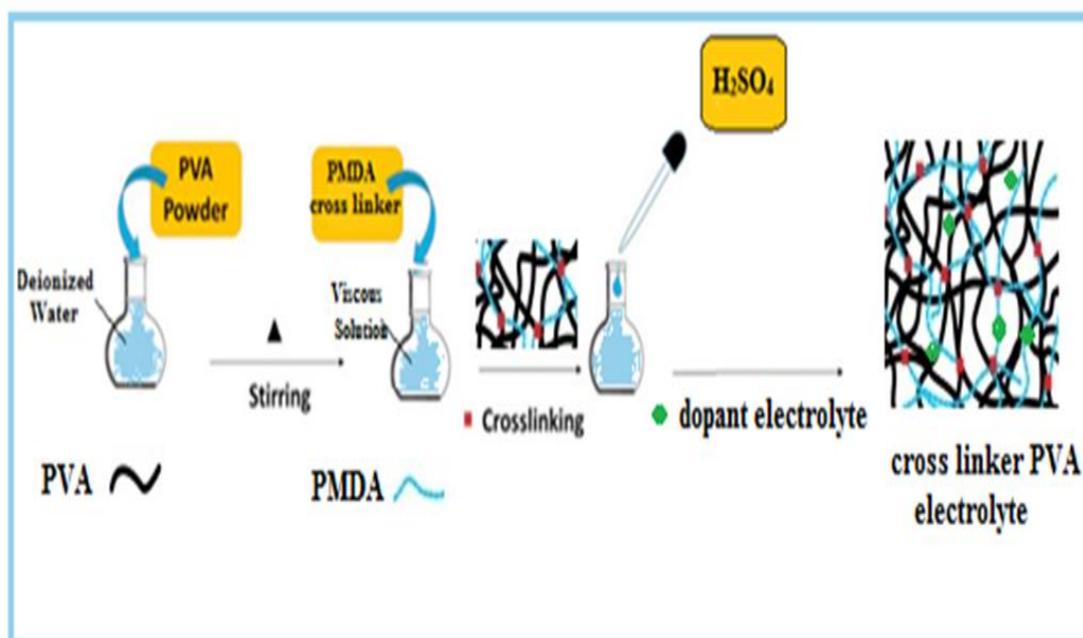
## 1. Introduction:

Poly Vinyl Alcohol (PVA) is one of the few semi-crystalline water-soluble synthetic polymers. Due to its extensive properties such as cost-effective, high hydrophilicity and favorable chemical cross-linking ability, it is a desirable candidate for solid polymer electrolyte and fuel cells[1]. Its high affinity to water is due its own strong hydrogen bonds between hydroxyl groups in PVA chains [2]. And because of its high hydrophilicity, PVA thin films generally exhibit weak stability in aqueous solutions at long term operations, moreover it has low ionic conductivity[3]. To solve this issue, the polymers chemical structure can be modified by cross-linking, hybridization or grafting. Cross-linking of the hydroxyl groups of the PVA can decrease the value of water uptake and control swelling ratio [3,4].

PVA modification by controlling crosslinking of its hydroxyl groups opened up new fields of usage for this polymer[5]. All multi-functional compounds such as dialdehydes, dicarboxylic, dianhydrides, etc that are able to react with hydroxyl group have been tried for PVA modification.[6].

Polymer electrolytes were commonly researched. Unfortunately, those polymer electrolyte types have exhibited low electrode-electrolyte contact or insufficient mechanical stability, thus, were deprived of the general efficiency [7]. In order to improve ionic conductivity of the PVA film, sulfuric acid was used as sulfonating as well as cross-linking agent [8]. Note that this study is highlighted the important of use solid polymer electrolytes (SPEs) as a conducting films in the field of polymer electrolyte[9]. Using Pyromellitic dianhydrides (PMDA) with PVA as a solid polymer electrolyte have achieved crosslinked networks containing polar carboxyl groups from dianhydride molecule and more crosslinking obtained between free carboxyl-hydroxyl groups in PVA chains, which enhance electric properties of PVA.

In the present paper, a solid polymer electrolyte base on PVA was investigated. Moreover, pyromellitic dianhydride was used for the crosslinking mechanism of PVA film. The ionic conductivity was enhanced using H<sub>2</sub>SO<sub>4</sub> with different molarities. Several techniques were used to characterize the prepared film (FTIR spectra, dielectric and electric test).



**Figure 1-**Cross-linking mechanism of the PVA by pyromellitic di-anhydride.

## 2. Experimental:

### 2.1 Materials and Methods:

Poly(vinyl alcohol)(PVA), Sulfuric acid and pyromellitic dianhydride (PMDA) were purchased from Sigma-Aldrich Co., U.S. A, as listed in Table 1.

**Table 1-** List of materials used for the preparation of polymer electrolyte

Materials		Molecular Weight (g/mol)	Supplier
Polymer	Poly(vinyl alcohol) (PVA)	145,000	Sigma-Aldrich (USA)
Ionic conductor	sulfuric acid (H <sub>2</sub> SO <sub>4</sub> )	98.08	Merck Millipore (Germany)
Cross-linking agent	Pyromellitic dianhydride (PMDA)	218.12	Sigma-Aldrich (USA)

### 2.2 Preparation of pure PVA films:

pure PVA film was prepared by dissolving 0.75 gm PVA in 15.0ml of deionized water under magnetic stirring at 30 °C for 1hour. Then the PVA aqueous solution was doped with 2 drops (about 0.1 ml)of (5 and 9) M sulfuric acid H<sub>2</sub>SO<sub>4</sub> and then cast onto a petri dish. The fabricated films were dried at room temperature for four days.

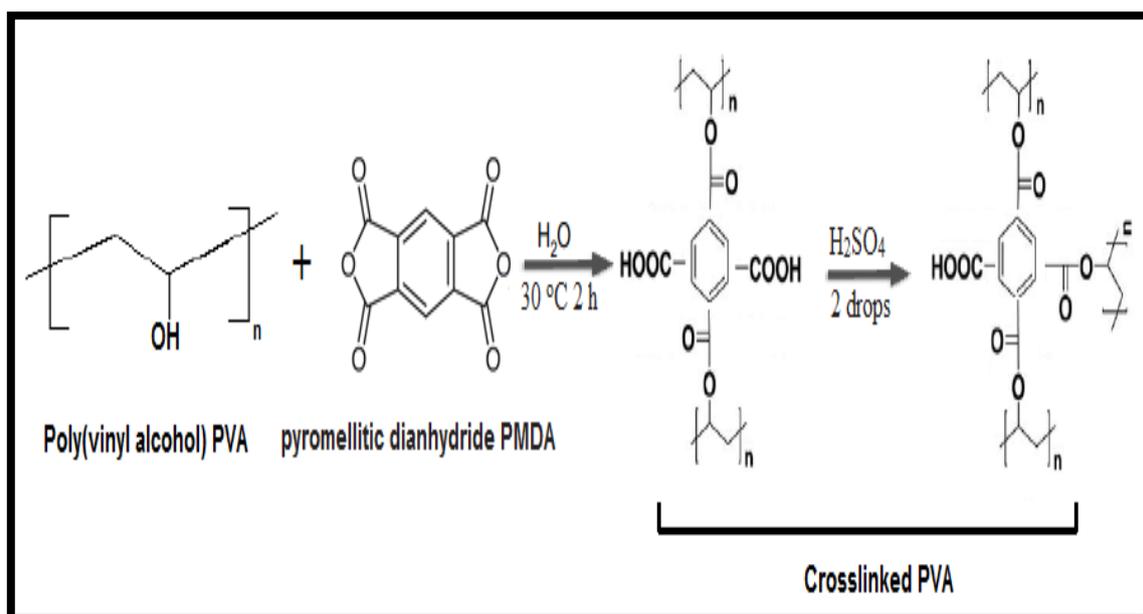


Figure 2-Schematic illustration of PVA/PMDA crosslink doped by  $H_2SO_4$

### 2.3 Preparation of pyromellitic dianhydride crosslinked PVA films:

Pyromellitic dianhydride (PMDA) cross-linked PVA films were prepared with the same process as that of pure PVA film. The cross-linking mechanism was done by adding  $PVA_x$  to  $PMDA_y$ , where  $x = 0.75$  gm and  $y = (0, 5, 10, 15, 20)$  wt% of  $x$ , and dissolving it in 15 ml of deionized water, followed by adding 2 drops of sulfuric acid under magnetic stirring at  $30\text{ }^\circ\text{C}$  for 2 Hrs. Figure 1 illustrates the cross-linking mechanism of the PVA by PMDA. Figure 2 shows schematic illustration of PVA/PMDA crosslink doped by  $H_2SO_4$ . The FTIR spectra were recorded with FT-IR Shidzu spectro-photometer (Japan) of wave number range ( $4,000\text{--}500$ )  $\text{cm}^{-1}$ .

Scanning Electron Microscope (VEGEA3 TESCAN, mode SE) was used to determine the thickness of PVA film which was about  $72.36\text{ }\mu\text{m}$ . Resistance and capacitance were measured with an LCR meter (model:HEP- 4775) at frequency range between (1-100)kHz.

### 3. Result and discussions:

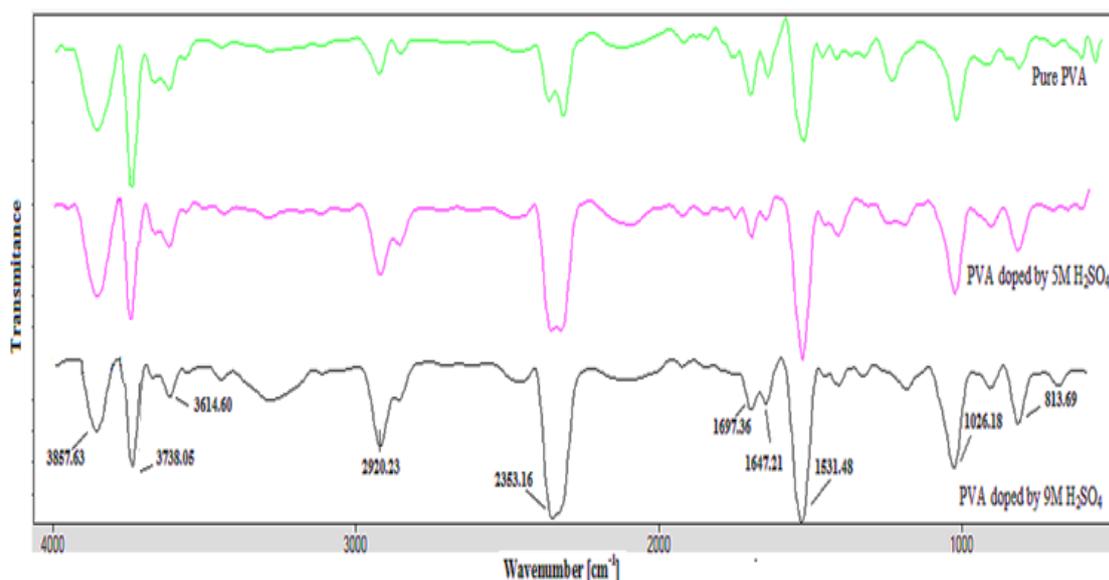


Figure 3- FT-IR spectra of pure PVA and PVA doped with 5M and 9M  $H_2SO_4$

Figure 3 shows the FT-IR spectra of pure PVA and PVA doped with 5M and 9M H<sub>2</sub>SO<sub>4</sub>. The strong O-H broad band observed at 3738.05 and 3857.63 m<sup>-1</sup> may be assigned to stretching due to the strong hydrogen bond of intramolecular and intermolecular type in PVA film [10]. The C-H stretching vibration was observed at 2920.23 cm<sup>-1</sup> [1].

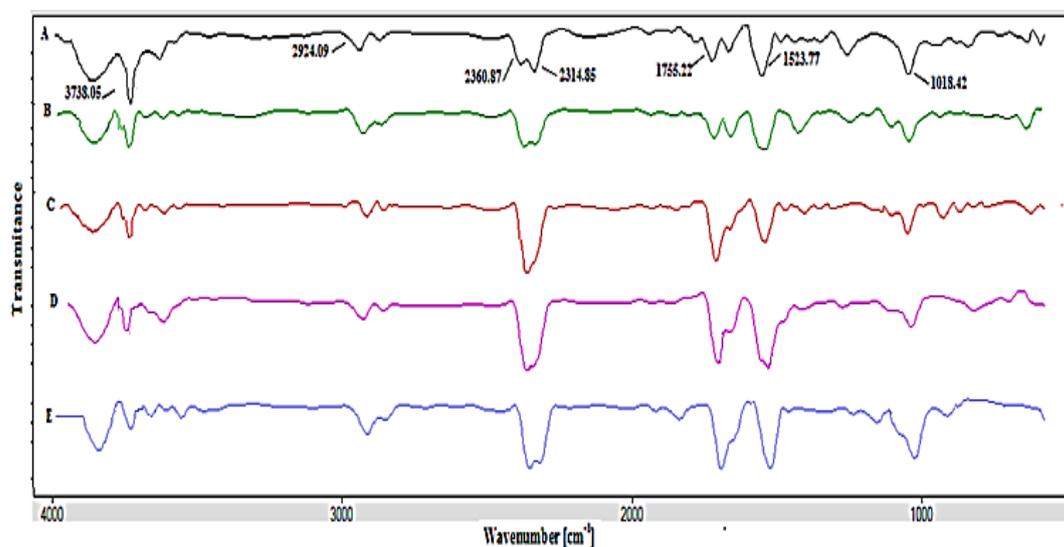
The peaks at 2353.16 and 1531.84 cm<sup>-1</sup> may be due to the stretching vibration of C=O and C-O of the residual non-hydrolyzed acetate group in the PVA molecular chain [10,11].

When PVA was doped with 5M and 9M H<sub>2</sub>SO<sub>4</sub>, a new peak was noticed at 813 cm<sup>-1</sup>. This peak may be due to the formation of hydrogen bond between the carbonyl (C=O) group from PVA and the H<sup>+</sup> ion from the H<sub>2</sub>SO<sub>4</sub> [10]. One can see that the main peaks at 3738.05 cm<sup>-1</sup> have become weaker compared with that of the pure PVA; this was due to the elimination of water and hence the fall in hydroxyl content. This result is in agreement with that of Gohil et al.[1].

In addition, H<sub>2</sub>SO<sub>4</sub> as a catalyst was used to accelerate the rate of cross-linking reaction. The C-H stretching vibration band at 2920.23 cm<sup>-1</sup> has changed its nature and a peak at 1697.36 cm<sup>-1</sup> indicates the generation of a -C=C- structure in the PVA chains [12].

Crosslinking increased when more PMDA was added as shown in Figure 4. As the PMDA concentration increases, more -OH groups of the PVA molecules react with the -COOH group of the hydrolyzed PMDA crosslinked, and the peak intensity of the O-H band at 3738.05 cm<sup>-1</sup> gradually decreases. This behavior was due to the decrease in concentration of the hydroxyl groups. After the occurrence of the cross-linking reaction, the peak was shifted towards higher wave numbers due to the bond formation between -COOH of anhydride and -OH group from PVA, as a result of the interaction between the hydroxyl groups and the cross-linker anhydride. This agrees with the results of Rasheed and Kareem [6] and Xu et al. [12].

In addition, another two characteristic bands at 1755.22 cm<sup>-1</sup> and 1018.42 cm<sup>-1</sup> were assigned to -C-O-C- asymmetric and symmetric stretching vibration of anhydride with PVA chain, respectively[3,13].



**Figure 4-**FT-IR spectra of A) pure PVA and PVA crosslinked with 5,10,15 and 20 wt.%PMDA for B,C,D and E respectively.

The a.c. conductivity ( $\sigma_{a.c.}$ ) was calculated from the relation [14]:

$$\sigma_{a.c.} = \epsilon_o \omega \epsilon' \tan \delta \quad (1)$$

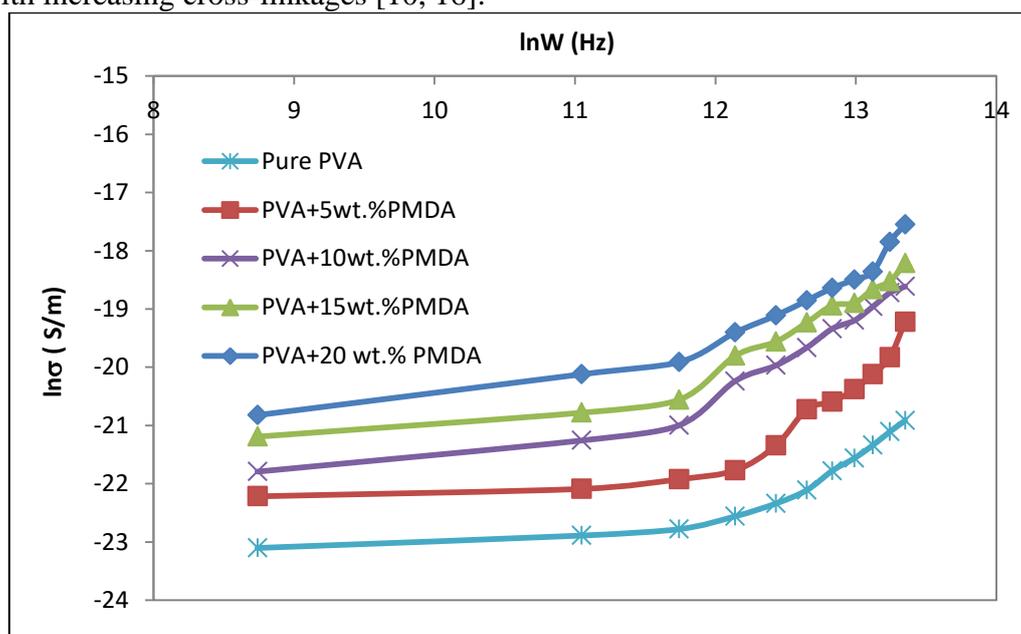
where  $\epsilon_0$  is the permittivity of free space  $8.85 \times 10^{-12}$  (F/m),  $A$  ( $m^2$ ) is the area of the electrodes and  $d$  (m) the thickness of the sample,  $\tan \delta$  is the dielectric dissipation factor and  $\omega$  is the angular frequency(Hz). Figures (5, 6 and 7) show that  $\sigma_{a.c}$  increases with the increase of frequency. Hence, there are two factors that influence  $\sigma_{a.c}$  which are ions motions and main chain motion of polymer backbone. It is related to the electronic polarization effect in the transport of charge carriers by hopping through defect sites along the chains [3].

FTIR spectra specifies that the chemical interaction occurred between the PVA and the acid dopant, which is why the hydrogen ion ( $H^+$ ) may easily be separated from carbonyl group to be free to move and this explains the proton conductivity of PVA [12].

From Figures (5,6 and 7), it can be noticed that there has been an increase in the ionic conductivity, also the number of free  $H^+$  ions has increased with the increase of the acid molarity. This behavior is supported by an increase in the C=O band intensity [13]. Conduction occurs via hopping mechanism when  $H^+$  ions hop from one site to another, leaving a vacancy that will be filled by another  $H^+$  ion from a neighboring site and may result in the exchange of ions between complex sites [10].

The sulfuric acid give active anions that have the ability of acting as donors as well as acceptors in the transfer of the ions. The increase of the conductivity is a result of the presence of the excess acid in the polymer matrix[11, 15].

As observed from these figures, the increase of PMDA concentration increased the length of the polymer chain of the PVA films which increased free volume and ionic mobility in the film with increasing cross-linkages [10, 16].



**Figure 5-**  $\ln(\sigma)$  as a function of frequency for PVA/PMDA crosslinking without doping by  $H_2SO_4$

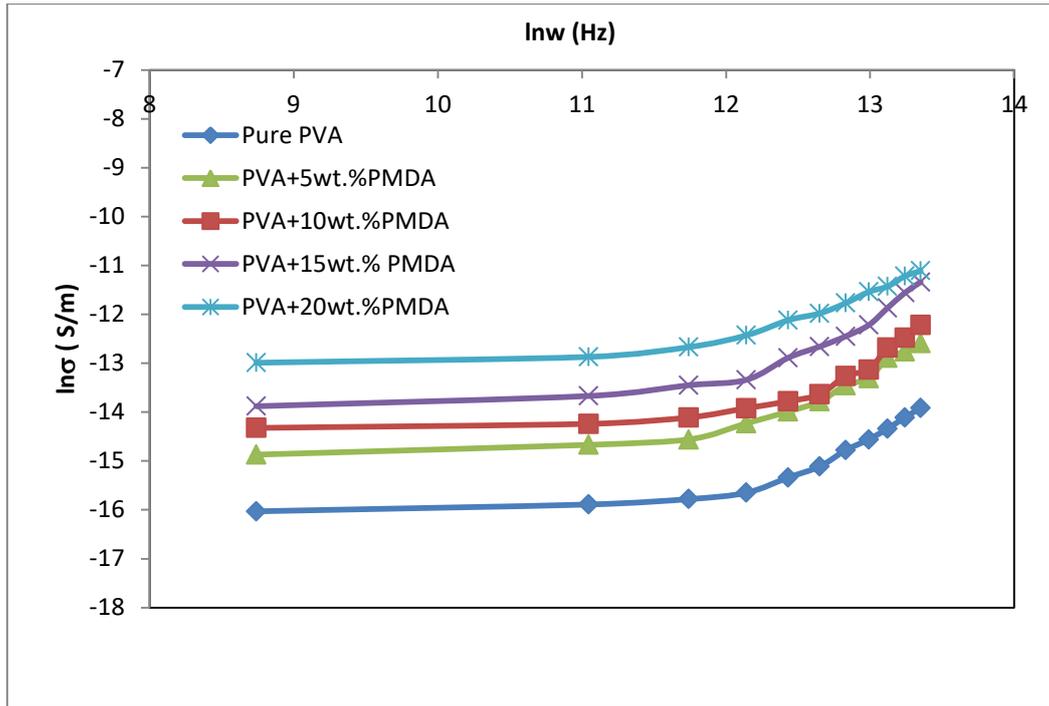


Figure 6- $\ln(\sigma)$  as a function of frequency for PVA/PMDA crosslinking doped by 5M  $H_2SO_4$

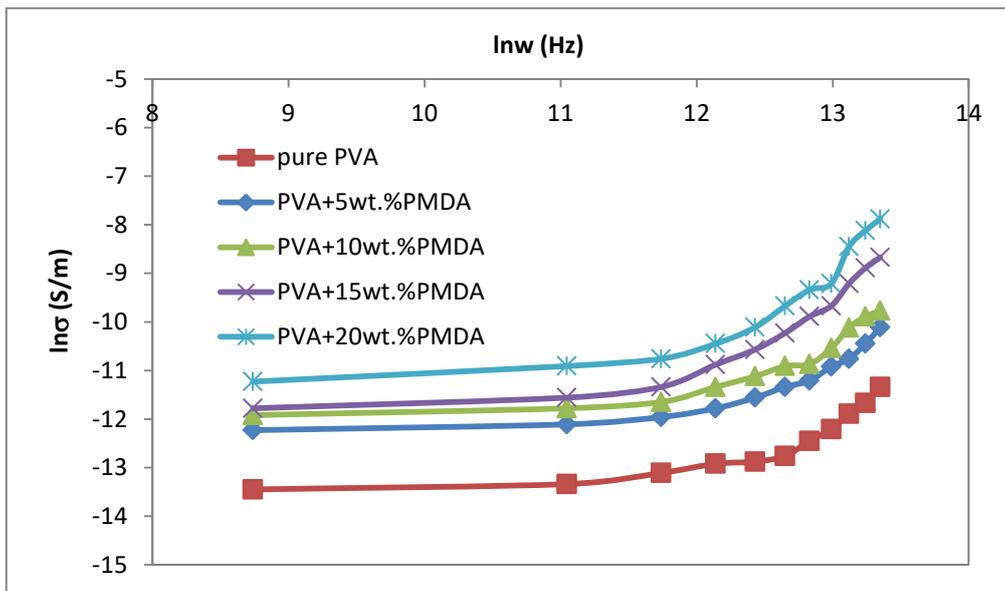


Figure 7- $\ln(\sigma)$  as a function of frequency for PVA/PMDA crosslinking doped by 9M  $H_2SO_4$

The dielectric behavior of the crosslinked PVA was studied terms of different parameters. Dielectric constant ( $\epsilon'$ ) of composite was calculated by the following relation:

$$\epsilon' = C/C_0 \tag{2}$$

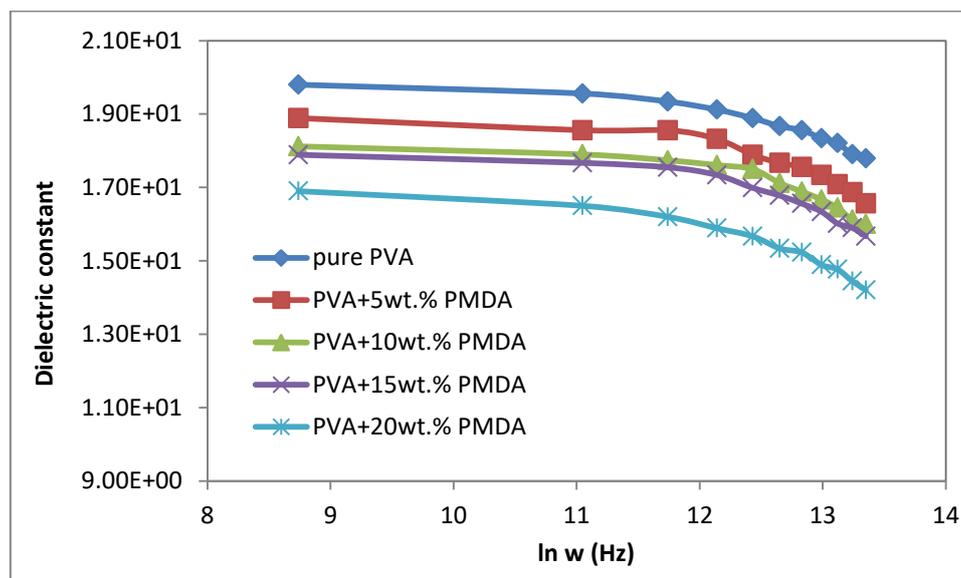
where C and  $C_0$  are the capacitance with and without dielectric, respectively;  $C_0$  in F is given by Rasheed and Kareem[14]:

Figures ( 8, 9 and 10) show the dielectric constant variation with frequency for different PMDA concentration(5,10,15 and 20)wt.% with and without doping with  $H_2SO_4$ . It is observed from the figures that the dielectric constant decreased rapidly at high frequencies. This was due to the reduction of space charge polarization effect and could be explained by the tendency of dipoles which will hardly be capable of following the field of variation at

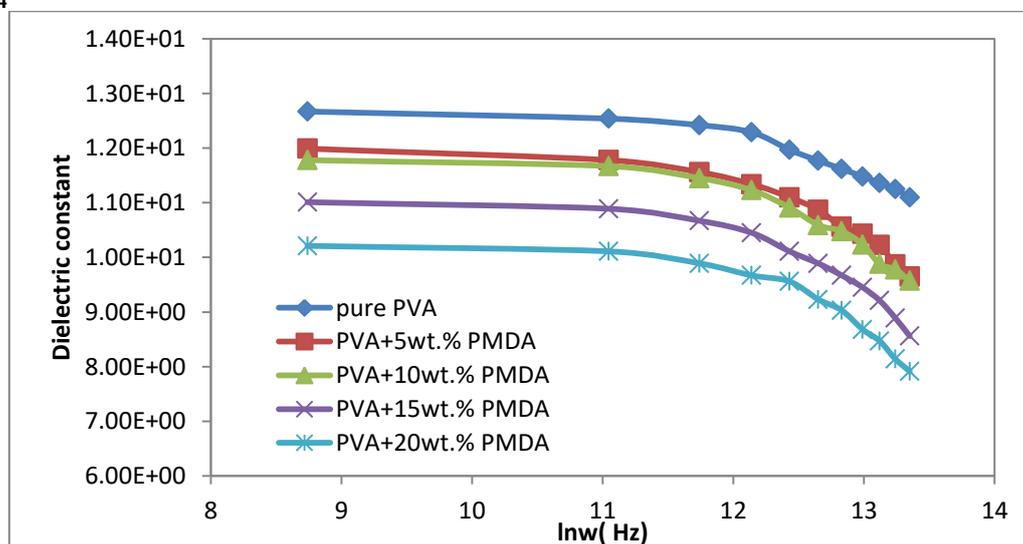
higher frequency values [17]. At relatively low frequencies, the films have shown a high value of the dielectric constant, and this has been associated with the electrode polarization of the polymer. This agrees with the findings reported by Badr *et al.*, [16].

The sample with 20wt.% PMDA showed low dielectric constant values. This can be understood in terms of the degree of crosslinking and changes in crystallinity [18,19].

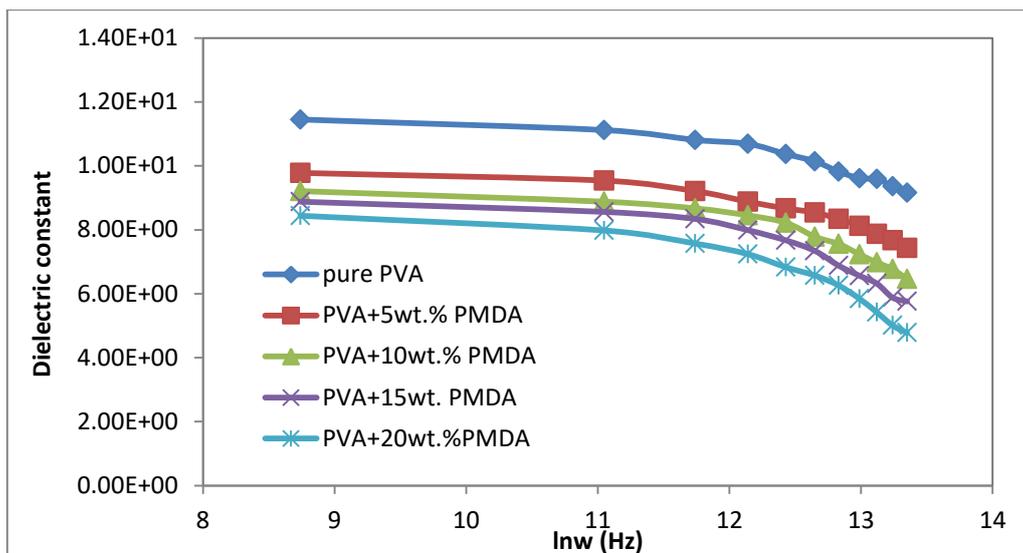
Crystallization results in the prevention of movement of polymer chains; the phase of the crystalline is rigid and it does not show any processes of dielectric relaxation, thus, the dielectric response is lower [18].



**Figure 8-**Dielectric constant for pure PVA and PMDA crosslinking without doping by  $H_2SO_4$



**Figure 9-**Dielectric constant for pure PVA and PMDA crosslinking doped by 5M  $H_2SO_4$



**Figure 10**-Dielectric constant for pure PVA and PMDA crosslinking doped by 9M H<sub>2</sub>SO<sub>4</sub>

H<sub>2</sub>SO<sub>4</sub> molarity dependence of the dielectric constant ( $\epsilon'$ ) at chosen frequency values are shown in Figures (8, 9 and 10). From the graphs,  $\epsilon'$  decrease with the increase in the H<sub>2</sub>SO<sub>4</sub> molarity for each frequency. As the H<sub>2</sub>SO<sub>4</sub> molarity increases, the number of ion charges in the films increases [20-23].

#### 4. Conclusions:

The new type PVA crosslinked with pyromellitic dianhydride doped with small volume of high molarity of H<sub>2</sub>SO<sub>4</sub> can be effective for future applications of solid polymer electrolyte in electrochemical devices.

In summary, cross-linked PVA films with different PMDA concentrations were compared with different molarity of H<sub>2</sub>SO<sub>4</sub> in order to enhance the ionic conductivity.

FTIR spectra specified that chemical interaction occurred between the PVA and dopant acid, thus, the hydrogen ion (H<sup>+</sup>) may be easily separated from the carbonyl group and free to move and this explains proton conductivity of PVA.

Increased cross-link density resulted in the reduction of water uptake and the increase of proton conductivity. 20 wt.% cross-linked film was found to be ideal due to the enhanced ionic mobility with reduction of the films pore size. In addition, this sample showed low dielectric constant values. As the H<sub>2</sub>SO<sub>4</sub> molarity increased, the number of ion charges in the films increased which caused increased ionic conductivity and decreased of the dielectric constant.

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