

Electrical and Swelling Study of Different Prepared Hydrogel

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Abstract Six different hydrogel prepared and characterized with FT-IR, the thermal stability with TG analyzer, swelling properties, the real and imaginary permittivity and the Ac conductivity of hydrogels films with LCR meter studied. The hydrogels PgA show better swelling, thermal stability and Ac conductivity values than the others hydrogel. These results may be due to the existence of the double bonds and the –COOH groups in the molecules structure of the PgA hydrogel more than the other prepared hydrogels.

Keywords Hydrogel permittivity, Swelling, Hydrogel, Chitosan, Pectin, Poly (vinyl alcohol), Conductive hydrogel

1. Introduction

Polymers hydrogel were increased attention in many application areas, including the medical field may be as a carrying and release for drugs. The term hydrogel may describe in three-dimensional network structures obtained from a class of synthetic and natural polymers which can absorb and keep significant amount of water [1, 2]. Hydrogels were classified into two categories: chemical gel was with covalently cross-linked. Physical gel: the networks were held together by molecular entanglements, ionic forces, hydrogen bonding or hydrophobic interactions. In this cross-linked gels were present (physical interactions), which exist between different polymer chains. Between these polymer chains were took place the swelling of Hydrogels in response to environmental changes such as temperature, pH, electric field, radiation, etc., are promising as smart materials [3]. Drugs were show an increasing interest in various biomedical, industrial and agricultural applications [4-15]. The swelling properties of the gel were very important and highly dependent on the chemical structure of the gel [16-18]. The hydrophilicity of the network was due to the presence of chemical residues, such as hydroxyl (-OH), carboxylic (-COOH), amide (-CONH-), primary amide (-CONH 2), sulfonic acid (-SO₃H), and others can found in the polymer backbone. Nevertheless, it was also possible to hydrogels produce a significant portion of hydrophobic polymer, by blending or polymerization of hydrophilic and hydrophobic polymers hydro. With these conditions could be the water retention in the hydrogels and appropriate to the drug

diffusion [19], many hydrogel-based networks developed and manufactured as an intelligent carrier of drugs [20-21]. A different type of electro-responsive hydrogel reported [22, 23]. In polycationic and polyanionic solutions mixture were formed via ionic bonding between the positively charged ions like NH³⁺ groups and negatively charged like COO, SO₃ ...etc. groups. Complexes textures were formed due to the hydrogen bonding [18]. The mixtures of two or more polymers could make a polymer composite. It was well known that composites can be produced exhibiting enhanced properties that the constituent materials may not exhibit [24-26]. The interface properties were affected the characteristics and performance of these composites [27]. One of the most attractive features was their dielectric properties could be widely changed by choice of shape, size, and the conductivity of filled constituents in the polymer; most of the interesting properties of polymers were the complex motions within their molecular matrix [28]. The polymeric interfaces act as charge-carrier [29]. Therefore, it has become essential to show the effect of interfaces on transport, storage and the charge-carrier generation in polymeric systems. The study of dielectric constant and dielectric loss, as a function of frequency was one of the most convenient and sensitive methods of studying polymeric structure, for polymer composites in the solid or viscoelastic state, the physical structure was of great importance in determining the dielectric behavior [30]. The electrical response of a normal dielectric can be described by its conductance, dielectric constant and loss factor.

Our target in this work was to investigate the electrical properties of many prepared hydrogel polymer composite, dielectric constant and dielectric loss, as a function of frequency, the electrical conductivity and the thermal stability with swelling.

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2. Experimental

2.1. Materials

Chitosan (C), medium average molecular weight, poly(vinyl alcohol) (PVA) 72000 molecular weight, glutaraldehyde solution (25%), glacial acetic acid, maleic anhydride, Acrylamide (AM), pectin and maleic anhydride (from Sigma–Aldrich), sulphuric acid (from ROMIL LTD), acrylic acid (AA, from HIMEDIA), ammonium persulphate (APS from Hopkins & Williams LTD), TEMED (from HIMEDIA), N,N-methylenebisacrylamide (MBA, from Thomas beaker) and potassium persulphate (KPS, from Fluka) were used as received. All chemicals were of analytical grade except pectin. Double distilled water was used in all preparation and swelling measurements.

2.2. Instrumentals

FT-IR spectra were recorded by using Shimadzu, (FT-IR)-8300, Infrared Spectrophotometer in the range (4000 – 400) cm^{-1} . DSC & TGA were made with DSC/TGA, STA PT-1000 LINSEIS, LCR Electronic Test device is used to measure the Inductance (L), Capacitance (C), and Resistance (R) of a component measured by using Hewlett-Packard LCR Meter model 4274A device.

2.3. Preparation of Hydrogels

Many hydrogel were prepared with different cross linking agent and methods and as following the hydrogel singed.

1. The symbol (CPG) represented to the hydrogel {polyvinyl alcohol (PVA) solution with chitosan (C) and glutaraldehyde (G) as crosslinking agent}.
2. The symbol (CPM) represented to the hydrogel {PVA with chitosan (C) and maleic anhydride (M) as crosslinking agent}.
3. The symbol (PPM) represented to the hydrogel {PVA and pectin (P) and maleic anhydride (M) as crosslinking agent}.
4. The symbol (PgA) represented to the hydrogel {graft co-polymerization of acrylic acid (Pg) on PVA}.
5. The symbol (CgA) represented to the hydrogel {graft co-polymerization of acryl amide on chitosan}.
6. The symbol (IPN) represented to the hydrogel {co-polymerization of acryl acid and acryl amide in presence chitosan}.

The PVA solution (10%w/v) was prepared by dissolving 10g of PVA in 100ml distilled water with stirring at 70 °C. Chitosan solution (1%w/v) was prepared by dissolving 1g of chitosan in acetic acid solution (1%) with stirring at 60 °C, and Pectin solution (2.5 %w/v) was prepared by dissolving 0.5g of pectin in 20ml distilled water with stirring at 50 °C.

Preparation CPG and CPM hydrogels:

CPG and CPM hydrogels were prepared by mixing equal volumes of PVA solution with chitosan solution. The mixture was stirred constantly until homogeneous at 60 °C and appropriate amount of crosslinking agents (0.3g of

maleic anhydride in CPG hydrogel or 10 ml of glutaraldehyde solution (1.25%) in CPM hydrogel) were added into the mixture under constant stirring with 2 drops of H_2SO_4 concentration [31, 32].

Preparation PPM hydrogel:

PPM hydrogel was prepared by mixing equal volumes of PVA solution with pectin solution. The mixture was stirred constantly until homogeneous at 60 °C and 0.3g of maleic anhydride as crosslink agent was added into the mixture under constant stirring with 2 drops of glacial acetic [33].

Preparation PgA hydrogel:

PgA hydrogel was prepared by mixing 20 ml of PVA solution with 0.0375 g of potassium persulphate (KPS) as initiator and 3.8 ml of acrylic acid under N_2 shielding with 0.0375 g of N, N'-methylene bis acrylamide (MBA) as crosslinker [34].

Preparation CgA hydrogel:

CgA hydrogel was prepared by mixing 20 ml of chitosan solution with 0.07 g of ammonium persulphate (APS) as initiator and 1g of acrylamide under N_2 shielding at 60 °C with 0.07g of N, N'-methylene bis acrylamide (MBA) at same temperature with stirring [35].

Preparation IPN Hydrogel:

IPN Hydrogel was prepared by free radical polymerization of acrylamide (AM) and acrylic acid (AA) in presence of the chitosan (CHI). The mass of AM and AA were determined with ratio (CHI/AA/AM) equal to (10/10/80 w%) together with MBA (3.3×10^{-2} mol/L), APS (1.2×10^{-3} mol/L) and TEMED in a 1:1. Than a molar ratio with APS was append to a 1% chitosan solution in 1% acetic acid and stirred for 10 minutes at room temperature under shielding N_2 . Finally, it was placed in a water bath at 50 °C for 6 h. [36]. All reaction mixtures after enough mixing were formed the hydrogels then poured in to mold and left it to dry in air. The hydrogel products were dried at 40 °C in a vacuum oven overnight. The whole mass converted into a transparent film and it was purified by equilibrating it in double distilled water for a week.

2.4. Swelling of Hydrogels

Swelling studies were carried out for all the hydrogels. Hydrogels were drayed with vacuum oven for 20 hours at 60 °C and weighed and placed than into 100 mL of water at room temperature. At time intervals, gently wiped with a tissue to remove surface water, reweighed, and then placed back into the water vessel as quickly as possible. The mean weights were determined for each formulation, and the degree of Swelling (S) was calculated at each time point according to the relationship [37].

$$S = \frac{Ws - Wd}{Wd} \quad (1)$$

Where Wd and Ws were the dry and swollen matrix

weights at immersion time (t) in the water, respectively.

2.5. Dielectric Constant Measurements with LCR Meter

The above fabricated films were cut in dry state in 2x1.5 cm pieces to fit a silver electrode to measure the real, imaginary permittivity and the AC conductivity properties using Precision LCR meter with frequency range of (100Hz-100 KHz).

The dielectric parameters as a function of frequency were described by the complex permittivity [39].

$$\varepsilon^*(\omega) = \varepsilon'(\omega) - \varepsilon''(\omega) \quad (2)$$

ε' and ε'' were the real part and imaginary part components of the energy storage and loss, respectively, in each cycle of the electrical field. The measured capacitance C was used to calculate the dielectric constant ε' , using the following expression,

$$\varepsilon' = \frac{Cd}{\varepsilon_0 A} \quad (3)$$

Where d was the thickness between two electrodes (film thickness), A was the area of the electrode, ε_0 was permittivity of the space which equals to $8.85 \times 10^{-12} \text{ F.m}^{-1}$, ω was the angular frequency ($\omega = 2\pi f$) and f was the applied frequency while dielectric loss.

$$\varepsilon''(\omega) = \varepsilon'(\omega) \cdot \tan \delta(\omega) \quad (4)$$

The (Ac) conductivity (σ_{Ac}) calculated by the following equation [5].

$$\sigma = \varepsilon_0 \varepsilon' \omega \tan \delta \quad (5)$$

3. Results and Discussion

3.1. FTIR Characterization of Hydrogels

The FTIR spectrum of the pure chitosan was shown in Figure 1. The spectrum showed a strong absorption band at 3429 cm^{-1} was due to OH and amine N-H symmetrical stretching vibrations. A peak at 2881 cm^{-1} was due to symmetric -CH₂ stretching vibration attributed to pyranose ring [39-42].

Peaks at 1654 and 1562 cm^{-1} were due to -C=O stretching (amide I) and NH stretching (amide II). The sharp peaks at 1423 and 1377 cm^{-1} were assigned to CH₃ in amide group [43]. The peaks at 1261 , 1319 cm^{-1} were assigned to C—N groups, peak at 1157 cm^{-1} was due to secondary alcohol. The broad peak at 1080 cm^{-1} was indicated the C-O stretching vibration in chitosan. The peak at 894 cm^{-1} was assigned to the structure of saccharide [44].

Figure 2. shows the FTIR spectra relative to the pectin. The spectrum showed broad peak at 3410 and 3294 cm^{-1} was due to the stretching of —OH groups and stretching of —NH amide. The peak at 2943 cm^{-1} indicated C—H stretching vibration. The strong peak at 1593 cm^{-1} was assigned to C=O (acidic) stretching vibration. The peaks at 1438 , 1423 and

1388 cm^{-1} could be -OH bending vibration peaks and assigned to -CH₂ scissoring, respectively. The peaks at 1280 , 1303 were assigned to C—N groups. The peak at 1149 cm^{-1} suggested the presence of —CH—OH in aliphatic cyclic secondary alcohol. The peaks at 1026 cm^{-1} was indicated the C-O stretching vibration in pectin [45, 46].

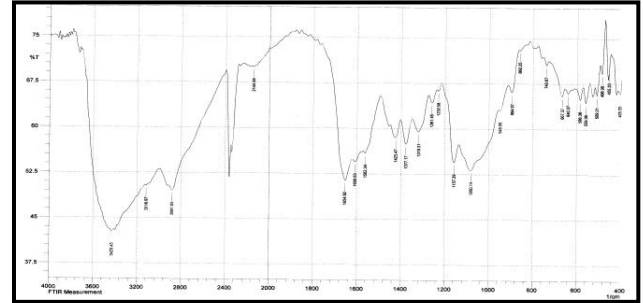


Figure 1. FT-IR spectrum of chitosan

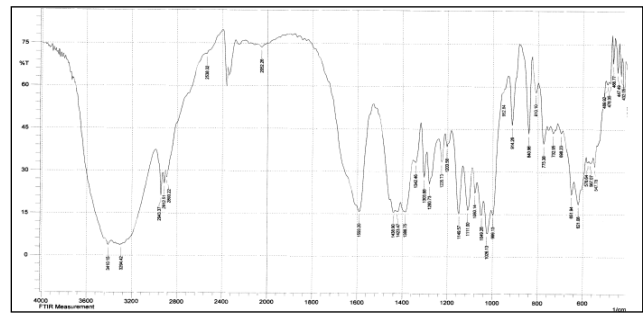


Figure 2. FT-IR spectrum of pectin

In Figure 3. shows the FTIR spectrum of PVA. The broad band observed at 3417 cm^{-1} was associated with the O—H stretching vibration. The vibrational band observed at 2939 and 2908 cm^{-1} were the result of the C—H stretch from alkyl groups and the peaks at 1712 , 1651 and 1141 cm^{-1} were due to the C=O stretches from the remaining acetate groups in PVA (saponification reaction of polyvinyl acetate) and C—O alcoholic [47, 48].

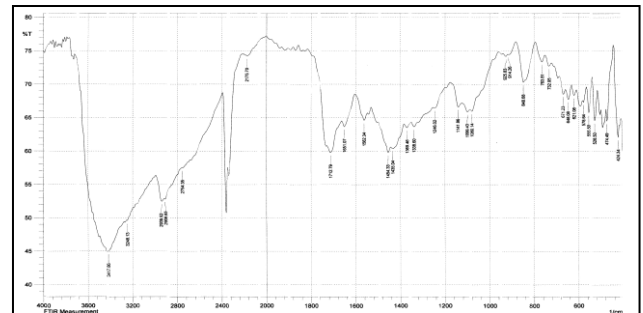


Figure 3. FT-IR spectrum of PVA

The figure 4. was represented of (PgA) film spectrum. The peak at 3402 cm^{-1} was returned to O-H stretching vibration of PVA. The peaks (2939 & 2908 cm^{-1}) were returned to C-H group stretching vibration and appeared also at the same frequency. The peaks were returned to C=O appeared stronger, sharper and shifted to 1724 cm^{-1} and 1643 cm^{-1} . The peak was returned to C-O alcoholic group stretching

vibration was appeared in same frequency at 1141 cm^{-1} and new peak was appeared at 1192 cm^{-1} returned to C-O group of acrylic acid. The New peak appearance at 1296 cm^{-1} was returned to C-N group of bis acryl amide. The new peak appearance at 1192 cm^{-1} was due to the formation of acetal ring, which confirm the grafting of PAA in to PVA [40]. Figure 5. shows the spectrum of (PPM film). The overlap broad peak returned to O-H and N-H groups stretching vibration was shifted to (3429 cm^{-1}). The peak was shifted to 2939 cm^{-1} returned to C-H stretching vibration. The peak was returned to C=O remaining acetate groups in PVA also appeared in the same frequency. The peak was returned to C=O stretching vibration to pectin was shifted to 1643 cm^{-1} with broader. The two peaks was returned to C-N groups stretching vibration were weaker and shifted to 1261 cm^{-1} for first peak and second peak at 1303 cm^{-1} disappeared. The peaks returned to C-O group stretching vibration was broader and shifted to 1066 cm^{-1} for pyranose ring in pectin and disappeared peaks at about 1149 cm^{-1} for cyclic secondary alcohol and C-O alcohol in PVA. This was suggested to get crosslinking between pectin and PVA with maleic anhydride [49].

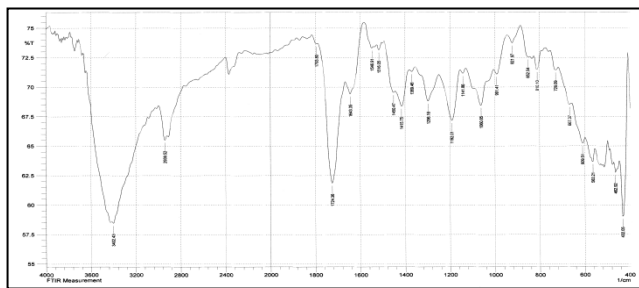


Figure 4. FT-IR spectrum of PgA film

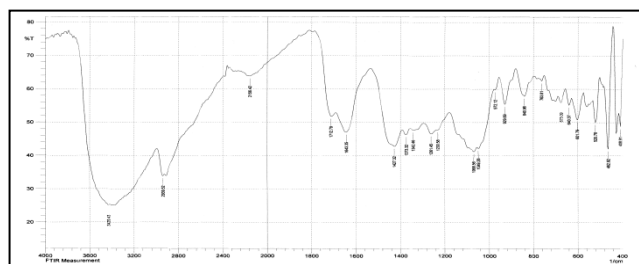


Figure 5. FT-IR spectrum of PPM film

Figure 6. show the spectra of (CPG film). The peaks were returned to O-H and N-H stretching groups stretching vibration were overlapped, sharper, and shifted to 3398 cm^{-1} . Two strong peaks at 2927 and 2858 cm^{-1} were returned to C-H stretching vibration. The peaks were returned to C=O disappeared. New peak was appeared at 1597 cm^{-1} was returned to Schiff base (C=N). This was explained to get chemical crosslinking of chitosan and PVA by glutaraldehyde. The imine group was formed by the nucleophilic reaction of the amine group from chitosan with the carbonyl group from glutaraldehyde. The two peaks were returned to C-N groups stretching vibration were weaker and shifted to 1246 cm^{-1} for first peak and second peak at 1319 cm^{-1}

cm^{-1} was disappeared. The peaks were returned to C-O ring in chitosan and cyclic secondary alcohol, alcoholic in PVA were shifted to 1045 and $1118, 1190\text{ cm}^{-1}$, respectively [50, 51].

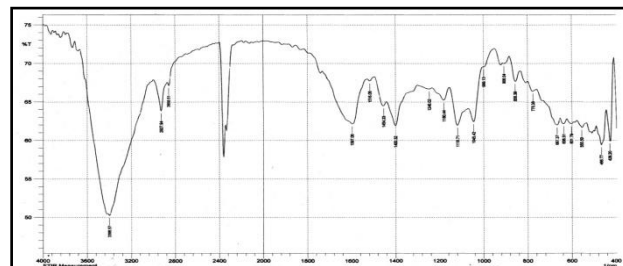


Figure 6. FT-IR spectrum of CPG film

Figure 7 shows FIIR spectra of CPM hydrogel film. The strong peak was returned to O-H group stretching vibration was appeared at 3433 cm^{-1} . The peak at 3398 cm^{-1} was assigned to N-H stretching vibration. The peak at 2943 cm^{-1} was assigned to C-H stretching vibration. The peaks were returned to C=O amide of chitosan and remaining acetate group in PVA was shifted to 1643 and 1705 cm^{-1} (weaker) respectively. The two peaks was returned to C-N groups stretching vibration were disappeared peak at 1261 cm^{-1} for first peak and second peak at 1319 cm^{-1} was shifted to 1319 cm^{-1} . The peak was returned to C-O ring in chitosan was shifted to 1087 cm^{-1} and disappeared peak for cyclic secondary alcohol and alcoholic in PVA.

From reaction mechanism expected to get interaction between O-H groups from PVA and carbonyl groups from maleic anhydride to form unsaturated ester, this represented with appearance peaks at 1643 cm^{-1} , 1705 cm^{-1} returned to CH=CH stretching and ester carbonyl, respectively. On the other may be form unsaturated amide by interaction between NH_2 groups from chitosan with C=O groups from maleic anhydride, this represented with appearance peak at 1550 cm^{-1} returned to amide carbonyl stretching [52, 53].

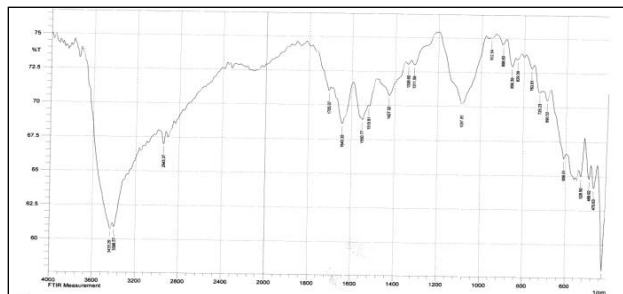


Figure 7. FT-IR spectrum of CPM film

The synthesis of chitosan-g-polyacrylamide hydrogel (CgA) film was confirmed by comparing its FTIR spectrum with the spectrum of chitosan Figure 8 The chitosan spectrum shows the characteristic absorption bands at 1654 cm^{-1} (amide) and 1562 cm^{-1} (amine). These two peaks have a minor shift and are broader in the hydrogel spectrum, which is reconfirmed by two peaks at 3190 and 1670 cm^{-1} correspond to the NH_2 primary amides and C=O amide

stretching vibrations, respectively. Moreover, the C–H and O–H bending vibrations are observed in the 1300–1400 cm^{-1} with a sharp peak at 1400 cm^{-1} . However, this sharp peak is related to the O–H group like two peaks at 1157 and 1080 cm^{-1} (alcoholic and etheric C–O stretching vibrations, respectively), which are decreased strength peaks in the hydrogel spectrum. This implies that the hydroxyl group of chitosan is the preferred site for the reaction with the crosslinker and the grafting of acrylamide due to lower steric hindrance of the primary hydroxyl group [54].

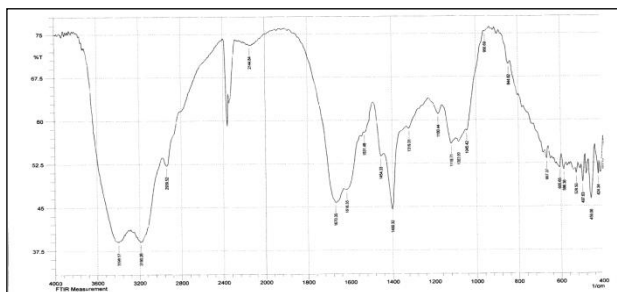


Figure 8. FT-IR spectrum of CgA film

Figure 9 show spectra of interpenetrated (chitosan-poly (acrylic acid-co-acrylamide) film. It shows the absorption band at 1720 cm^{-1} due to the C=O stretching vibration of the carboxylic groups in poly acrylic acid. The intense band at 1674 cm^{-1} corresponds to the C=O stretching vibration of amide group of poly acryl amide. The main absorption bands of the chitosan appeared also in this spectra [55].

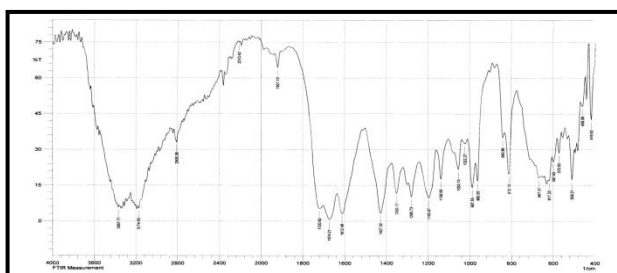


Figure 9. FT-IR spectrum of IPN film

3.2. Swelling Properties of Hydrogels

The favorable property of hydrogels was their ability to swell, when put in contact with a thermodynamically compatible solvent. The swelling properties, which usually used degree of swelling to define hydrogels, depend on many factors such as network density, solvent nature, polymer solvent interaction parameter.

The degree of the swelling S was increased with the time. Figure 10 was interpreted that the swelling increased with the time until the equilibrium state on the horizontal path. The prepared hydrogels took different periods to reach equilibrium point, this property was very important. The different hydrogels were show different degree of swelling value $\text{PgA} > \text{CPM} > \text{CgA} > \text{CPG} > \text{PPM} > \text{IPN}$, all these hydrogels were covalent cross linked, and consist –OH functional group in different ratios, thus was observed that maximum swelling for the PgA hydrogel greater than the

other hydrogels, this may due that PgA consisted free –COOH functional groups from the acrylic acid, These groups were made the high ability of swelling more than the other hydrogels [56, 57].

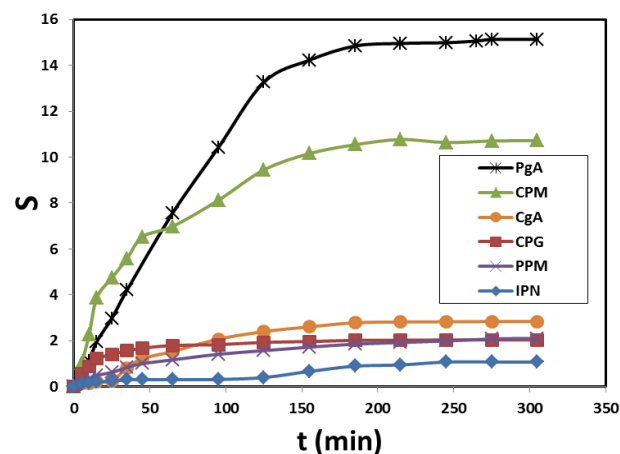


Figure 10. Degree of swelling of hydrogels

3.3. Thermal Analysis (TGA)

The heat decomposition of the hydrogels materials were studied with thermogravimetry, this study was illustrated the stability of the materials. In table 1 TGA data showed the thermal curve stability at 50% mass change of the prepared hydrogels. The thermal degradation was took a different steps of degradation to arrive the 50% of masse change, this may be depending on the ratio of cross linking and the nature of the materials. PGA and CgA were 50% mass decomposed at 398 and 415 $^{\circ}\text{C}$ respectively and show the better thermal stability then the other hydrogels.

Table 1. Thermal stability at 50% mass change

| Hydrogels | PgA | CPM | CpG | PPM | CgA | IPN |
|--------------------------------|-----|-----|-----|-----|-----|-----|
| Temperature $^{\circ}\text{C}$ | 398 | 225 | 245 | 355 | 415 | 385 |

3.4. Dielectric Constant Values

The material was determined in the first place by their polarization at a certain frequency. In multi-component systems were migrated the free charge carriers through the material, the space charges were reinforced at the interfaces of the composites components of the dielectric and conductive materials at the interfaces (this called interfacial polarization). Interfacial Polarization of Polymers can be identified with low frequencies permittivity measurements with Maxwell-Wagner-seller's method [58]. The Changes in the permittivity values as a function of frequency were attributed to dielectric relaxations particularly in the low-frequency, through small Brownian motion of the entire chain (segmental movements). However, these changes were also through interface polarizing type as Maxwell-Wagner - selling [59, 60]. The real and imaginary permittivity affected with different frequency values, these measurements data were shown good figures and consistent with the

interpretation of many reference [61, 62]. The figures 11 and 12 were show the difference in the real part of the permittivity with frequencies for all films. At low frequencies 100 Hz the permittivity reaches the highest values in all cases and rapidly decreased the (ϵ') with increasing of the frequency to 400 Hz. and stilled low. This made sense, since the low-frequency range was varying gradually the field that saves time and therefore induced dipoles to align themselves according to the applied field, thereby strengthening the polarization. A significant contribution to improve values of (ϵ') was especially in the low-frequency polarization interface and / or the electrode polarization, set pole polarization of the space charge accumulation in interfaces of poles [63].

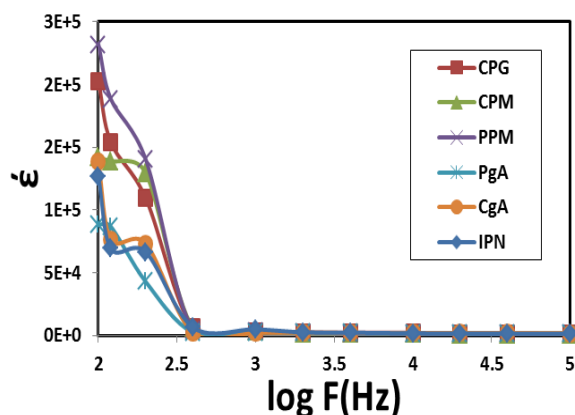


Figure 11. Real permittivity versus log frequency for hydrogels

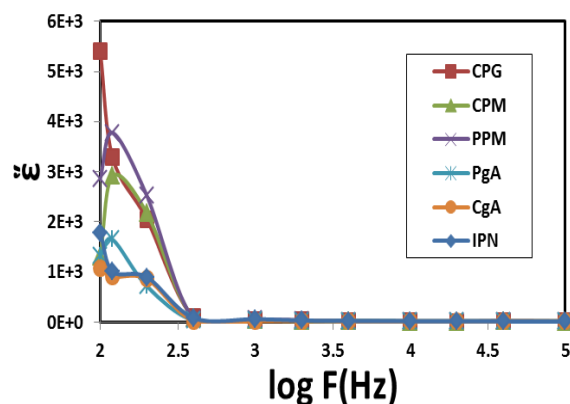


Figure 12. Imaginary permittivity versus log frequency for hydrogels

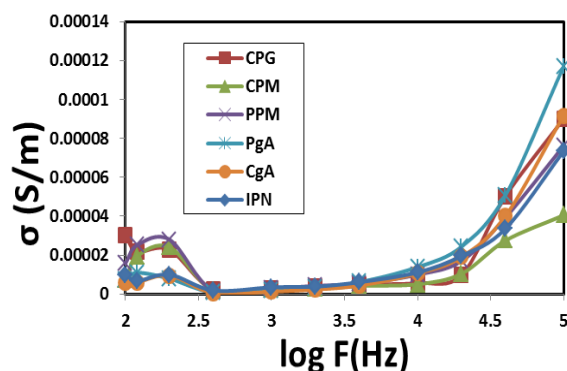


Figure 13. AC conductivity of the hydrogels versus with log frequency

Figure 13. was showed different behavior of the AC conductivity of the hydrogels generally, at high frequency 10^5 were all the hydrogel shown the largest value of the AC conductivity especially the PgA, this hydrogel may be included of many molecular double bonds more than the other hydrogel, the AC conductivity values were reduced gradually with decreasing of the frequency to 400 Hz. and shown the minimum values, the σ_{Ac} again shown slight increase with decreasing of the frequency to 100Hz. At low frequencies was the AC conductivity of the hydrogel PPM higher than the other at 200Hz.

4. Conclusions

Different types of hydrogels were successfully prepared with different methods. The results of the swelling and conductivity of the hydrogel were shown the PgA best hydrogel with good swelling and Ac conductivity, the $-\text{COOH}$ groups in the hydrogel molecular structure made the hydrogen bonds, which increased the swelling properties more than the others, on other hand the hydrogen bond and the double bonds in the PgA structure increased the conductivity. The thermal stability of PgA was good in comparison to other prepared hydrogel. The thermal stability may be due to good cross linking between the different polymer chain and/or to the nature of the prepared materials, if the cross linking was occurred in in PgA more than the other hydrogels and shown better swelling than the other this case need a future research.

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