Preparation of cross linked PVA with MA,EDTA,and a mixture of MA/EDTA for water uptake membranes at different pH

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Abstract

Poly (viny1 alcohol) (PVA) of 72000 g mol $^{-1}$ molar mass was cross linked through cold cast esterification with different mol % of MA and EDTA (10 % , 20 % and 30 %), and two different mol % mixture of MA / EDTA (20 %/5% and 20%/10%). Molecular structures of the produced membranes were identified by FTIR spectral analysis .

Mechanical measurements showed that, PVA cross linked with 30 mol% EDTA gave higher tensile strength value, while PVA cross linked with 30mol% MA gave higher elongation value at break.

Water swollen of the membranes was studied at ambient conditions and different pH solutions (4, 5, 6, and7) .

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Maximum swelling percent (S_w%) value at equilibrium was at pH7 for all membranes and this value decreases as pH was decreased.

Relation between maximum S_w% and the cross link density (ρ_c) was obtained mathematically to prove that the decrease in S_w% is due to the increase in ρ_c.

الخلاصة

تمت مشابكة بولي فاينيل الكحول ذو الكتلة الوزنية 72000غم/ مول بطريقة استرة الصب البارده مع حامض الماليك، اثلين ثنائي الأمين رباعي حامض الخليك بنسب مولية مختلفه (10%، 20% و30%) ومع مزيجين مختلفين من حامض الماليك/ اثلين ثنائي الأمين رباعي حامض الخليك بالنسب المولية (20%/5% و20%/10%). تم تشخيص التركيب الجزيئي للأغشية المحضرة بواسطة FTIR.

أظهرت القياسات الميكانيكية ان بولي فاينيل الكحول المتشابك مع 30مول % اثلين ثنائي الأمين رباعي حامض الخليك اعطى اعلى قيمة قوة شد بينما اعطى بولي فاينيل الكحول المتشابك مع 30مول% حامض الماليك اعلى قيمة استطاله عند القطع.

تمت دراسة سحب الماء بواسطة الأغشيه تحت الظروف الأعتيادية وعند قيم مختلفة لل pH(4,5,6,7). كانت اعلى نسبه لسحب الماء $S_W\%$ ولجميع الأغشية عندما تكون الـ PH (7) وان هذه القيمة تقل مع انخفاض الـ pH.

تم رياضياً معرفة العلاقه التي تربط كثافة التشابك العرضي ρ_c مع القيمة القصوى لـ $S_W\%$

لأثبات كون النقصان في $S_W\%$ يعزى الى الزياده في ρ_c .

INTRODUCTION

PVA is a polymer of simple chemical structure contains pendant hydroxyl groups and of various advantages, such as chemical stability and very good perm selectivity membrane in the symmetric and asymmetric mode [1, 2]. The basic property of PVA depends on its degree of polymerization and its degree **of hydrolysis; the % of hydroxyl groups in the molecule [3].**

PVA is hydrophilic and water soluble polymer of many interested properties and applications.

It can be used for absorbing water and swelling, as good biocompatible material, effective membrane in the separation of organic mixture, and good control release gel

[4-9].

The chemical modifications of PVA by esterification, oxidation, methylation, and cross linking are to improve its membrane activity and its chemical and mechanical properties of water dissolving resistant [10-12].

PVA can be cross linked by glutaraldehyde, acetaldehyde, formaldehyde, and dicarboxylic acids [13-17]. The cross linked structure has an effect on the diffusion of the molecules through the membrane because the increase in the mash size leads to an increase in the rate of diffusion [18].

There was wide study about the effect of the pH on the degree of swelling and on the compatibility to uptake water, that because these membranes contain groups that sensitive to H^+ or OH^- ion concentration, that depends on the type of the pendent groups which are acidic or basic and on their number in the chain [19-21].

In this study, PVA was cross linked with di and tetra carboxylic acids to prepare membranes of different cross linking density and contain C=C bonds, tert-amin groups, and both of these active positions to evaluate their tensile strength, elongation at break, and capability for water uptake (swelling) at different pH. That may be helpful to identify the most useful membrane for the extraction of water traces from solutions, it could be useful to extract traces of water from gasoline and other petroleum liquid products . and for other applications depend on the presence of C=C bond and tert-amine group and those depend on the mechanical behavior of these membranes.

Materials & Methods

Materials:

Poly (vinyl alcohol) PVA of Mw 72000 g/mol and degree of hydrolysis > 98% was purchased from Aldrich Chemical Co., maleic acid (MA) and ethylenediamine tetraacetic acid (EDTA) were supplied from Merck. All chemicals were used as received.

Preparation of membranes:

Membranes were obtained by the cold casting method. PVA solution (10% w/v) was prepared by dissolving the pre weighed PVA in distilled water with a constant stirring at 70-80℃ for more than 3h to get a clear solution. One drop of concentrated H_2SO_4 was added to PVA solution at room temperature followed by the addition of the required amount of cross linker with continuance stirring until the solution became homogeneous and free bubbles stopped. The resulting solution mixture was poured out into Petri dishes using a wide width knife with predetermined drawdown thickness and the casting thickness was controlled to be 0.4-0.45 mm. The reaction mixture left to dry for two days with a relative humidity of 25-30%. The dried membrane was peeled off and heated in oven at 80℃ for 1h to achieve thermally cross linking.

Infrared analysis:

The infrared (IR) spectra for the uncross linked PVA, PVA 10 mol l%MA, and PVA-10mol%EDTA membranes were measured with a Thermo Scientific Nicolet 380 Fourier transform infrared (FTIR) spectroscope. Each sample was dissolved in dimethyl sulfoxide and the IR for the solution was measured at room temperature.

Tensile and Elongation:

Tensile strength machine type Jianqiao Testing Equipment – China (Fig.1) was used to measure the tensile strength and elongation at break of PVA and its cross linked membranes. The sample thickness was measured using a micrometer at different locations and the mean thickness was calculated. Stripes used were of 0.4- o.45mm thickness and 8-10 mm length.

Water uptake (swelling):

The capacity of membrane to swell water was obtained by immersing the membrane of known weight in a distilled water of known pH at room temperature and the pH of the solution was controlled by 0.1N HCl. The membrane then taken out and wiped with a cleaning tissue to remove water from its surface and weighed quickly. The sample that immersed for 24h was dried in the oven and weighed to find any loss in weight. Each membrane was immersed for different times (2-24h) to obtain the maximum $S_w\%$ at equilibrium. $S_w\%$ was calculated from the following relation [22]:

$S_w\% = (W_s – W_d)/W_d \times 100$

Were W_s is the mass of the swollen membrane and W_d is the mass of dry membrane.

Results and Discussions

Preparation of membranes:

Different types of cross linked membranes were synthesized by esterification reaction between PVA and MA, EDTA, and a mixture of MA/EDTA. In the first two types ,PVA was cross linked with 10mol%, 20mol%, and 30mol% of each cross linker, while in the third type, PVA was cross linked with a mixtures of 20mol%MA/5mol%EDTA and 20mol%MA/10mol% EDTA. The esterification in each case was very slow and takes about two days followed by curing at 80℃ for 1h to obtain the solid phase. The cured membrane was boiled in water to remove out the unreacted cross linker. There was no weight change after the boiling process indicated there was no residual cross linker and the required mol% of the cross linker in each membrane was obtained .

The membrane thicknesses were in the range 0.4 -0.45 mm and their optical transparency was depends on the type and mol% of the cross linker. It was found that the transparency decreases as the mol% of the cross linker was increased. The transparency of PVA-EDTA membranes were less than those of PVA-MA membranes, that could be due to the variation in refractive index or to the difference in the orientation of anisotropic volume elements, or both, more than that, the domain size of the film increases as mol% of cross linker was increased and these domain sizes are smaller in PVA-MA membranes than in PVA-EDTA membranes leading to less scattered visible light from the surface of PVA-MA [23-25].

It was observed that the two membranes which were prepared from the cross linking of PVA with mixtures 20mol%MA/5 mol%EDTA and 20mol% MA/10 mol% EDTA were exhibited high compatibility between the two cross linkers in the same membrane, observed from the smoothness and homogeneity of their surfaces. These two membranes could be useful for applications need a membrane contains amine groups and C=C bonds in separated cross links. These applications are not investigated in this study.

Infrared analysis:

IR spectra for dimethyl solfoxide solutions of PVA-PVA10mol%MA, and PVA-10mol%EDTA were taken (Fig. 2-4). The broad peak at 3350-3370 cm^{-1} is corresponds to the –OH groups stretching and the peak at 2800-2875 cm^{-1} is the –CH stretching. The appearance of C=O stretching vibration at 1730 cm^{-1} (Fig.3) and at 1725 cm^{-1} (Fig.4) together with C-O bending at 1250 cm^{-1} indicated the a presence of ester groups and that proves the esterification reaction between some –OH groups of PVA and –COOH groups of the cross linker acids.

Tensile & Elongation:

Tensile strength (σ) was calculated from the following relation:

$\sigma = F/A$

Where F is the applied force per Newton and A is the cross-sectional area per mm^2 & Then σ unit is N/mm^2or MPa.

Tensile strength and elongation at break measurements of PVA and cross linked PVA are listed in (Table1). The results observed that both tensile strength and elongation at break were increased as the mol% of MA cross linker was increased, while the tensile strength increases and the elongation at break decreases as the mol % of EDTA cross linker was increased. This different effect of EDTA on the mechanical properties of the membrane was proved when EDTA and MA were presented together ass cross linkers in the same membrane which observed an increase in tensile strength and a decrease in the elongatio at break, that in comparison with the mechanical properties of PVA membranes cross linked with MA only.

This different in effect could be due to the capability of EDTA to make four ester links by one molecule and those strengths the membrane leads to an increase in the tensile strength and a decrease in the elongation at break. In the entire cross linked membranes, the cross links were decreased the freedom mobility of the PVA chains and that increases the membrane strength, but this effect in PVA-EDTA membrane was exceeded that for decreasing the elongation at break.

Water uptake (swelling):

Swelling measurement for each pure membrane was at room temperature and for a period of different immersing times (2,4,6, 8,10. and24h) in distilled water of different pH medium (4,5,6, and7). It was found experimentally that water absorption was increased with time and reaches equilibrium within 10h (Tables2-4), but the membrane was left in water for 24h to obtain any change in the weight after drying, but there was no change in the weight and that indicated there was not even partial solubility of the membrane in water at different pH and different times.

The swelling results showed a decrease in the Sw% as the mol% of the cross linker was increased and that was due to the decrease in the free volume and the number of hydrophilic (-OH) groups in the polymer backbone [7]. Also, the results were observed that sorption capability of PVA-EDTA membranes was higher than that for PVA-MA membranes, that could be due to the hydrogen bonded of amine groups with water through the nitrogen loan pair electrons in comparison with C=C bond in the MA backbone which not capable to make hydrogen bonds. Another reason for the more water uptake by PVA-EDTA membrane is the bigger size of EDTA molecule than MA molecule as cross linking agent;

EDTA contributes higher free volume to the membrane than MA.

It was well observed that the maximum Sw% (Table 5) for the different membranes was depends on the pH of the medium. As the pH decreases the concentration of H^+ ions increases and that more screened the hydroxyl groups of the PVA backbone and the nitrogen of the amine groups leads to a decrease in the capability of water molecules to undergo hydrogen bonding and that decreases Sw% (Fig.5-7), so,the higher maximum value of Sw% was at pH 7 for all the synthesized membranes.

Swelling and crosslink density :

The maximum swelling ratio (S_r) at equilibrium in water of pH 7 was used to calculate the average molar mass between two successive cross links (M_c) in the PVA cross linked membrane and to use this value to obtain the crosslink density (ρ_c). The following equations (1&2) were used by many researchers for the calculations [28-30].

$$\frac{1}{\bar{\mathrm{M}}\mathrm{c}} = \frac{2}{\bar{\mathrm{M}}\mathrm{n}} - \frac{\mathrm{V}-[1-\mathrm{Vr}]+\mathrm{Vr}+\mathrm{XVr}^2](1-\mathrm{Vr}^{2/3}\ \mathrm{N})}{\mathrm{Vw}\left(\mathrm{Vr}^{1/3}-\frac{\mathrm{Vr}}{2}\right)(1+\mathrm{Vr}^{1/3}\ \mathrm{N})^2} \qquad \ldots\ldots \quad 1$$

where $\overline{M}_n$ is the number average molar mass of uncross linked polymer, V is the specific volume of the polymer, V_r is the polymer volume fraction after equilibrium swelling, χ is the polymer-solvent interaction parameter, V_w is the molar volume of water (18.1 $cm^3/mol.$), and N is the number of bond vectors per chain which is equal to $2M_c/M_r$, where M_r is the molar mass of the monomer.

$\rho_c = 1/2\overline{M}_c$ …2

Basically, V_r is equal to $Vd_p/(Vd_p + V_{sw})$, where Vd_p and V_{sw} are the volume of un swollen dry) polymer membrane and the maximum volume of water in the membrane at equilibrium respectively, then:

$$V_r = \frac{\frac{Wd_p}{\rho_p}}{\frac{Wd_p}{\rho_p} + \frac{W_{sw}}{\rho_w}} \quad \text{….3}$$

Where Wd_p and W_{sw} are the mass of dry polymer and the maximum mass of water in the membrane at equilibrium respectively. ρ_p and ρ_w are the density of the polymer and water respectively.

The arrangement of equation (3) leads to:

$$V_r = \frac{1}{1 + \left(\frac{W_{sw}}{Wd_p}\right)\left(\frac{\rho_p}{\rho_w}\right)} \quad \text{….4}$$

where W_{sw}/Wd_p is the swelling ratio (S_r) which is equal to S_w% divided by 100 [31], hence,

$$V_r = \frac{1}{1 + S_r\left(\frac{\rho_p}{\rho_w}\right)} \quad \text{….5}$$

then equation (5) can be used to modify equation(1) to form equation (6) which is used for our calculations:

$$\frac{1}{\overline{M}_c} = -\frac{1}{2\rho_p V_w}\left[\frac{\ln(1 - V_r) + V_r + \chi V_r^2)}{\left(V_r^{\frac{1}{2}} - 0.5\, V_r\right)}\right] \quad \text{…..6}$$

The calculation from equation (6) was according to our assumptions that, the distribution of cross linking is random and the inter molecular cross linking are negligent.

The specific volume of uncross linked PVA is 0.788 cm^3/g [32], according to that its density (ρ_p) is 1.269 g/cm^3 and the PVA-water interaction parameter(χ) used in this calculation was 0.494 [26] . The calculated data from equations (6) and (2) are listed in (Table 6) .As can be seen from the obtained data, the ρ_c values of the network for the three systems were increased with increasing mol% of the cross linker (Figure 8) and that declared why the S_w% decreases in the same direction .

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Table(1) : Tensile strength and elongation at break for PVA and cross linked PVA at room temperature.

Sample	Tensile N/mm^2(MPa)	Elongation %
PVA	48	10.6
PVA-10 mol % MA	49.4	11.1
PVA-20 mol % MA	49.9	11.8
PVA-30 mol % MA	50.2	12.1
PVA-10 mol % EDTA	50.1	10.9
PVA-20 mol % EDTA	51.4	10.7
PVA-30 mol % EDTA	52.6	10.2
PVA-20 mol % MA/5mol % EDTA	50.2	11.7
PVA-20 mol % MA/10mol % EDTA	50.4	11.4

Table (2) : Water S_w% at ambient conditions and different pH by the cross linked PVA with different mol % MA.

	PVA-10mol%MA				PVA-20mol%MA				PVA-30mol%MA			
Time(h)	pH4	pH5	pH6	pH7	pH4	pPH5	pH6	pH7	pH4	pH5	pH6	pH7
2	129	134	139	145	109	115	118	122	99	105	109	112
4	138.2	140	144	152	116.5	120	122	125	106	107.5	113.2	116
6	142.5	143.4	148	157	120	123	125	128.5	112.1	113.5	117.5	118.2
8	144	148	153	161.2	123.5	125.5	128.5	131.6	118	118.6	120.1	121.1
10	145	149	154.2	162.1	125.5	125.1	130.6	131.8	118.6	119.7	121.2	121.8
24	145	149	154.2	162.1	124	125.1	130.6	131.8	118.6	119.7	121.2	121.8

Table (3) : Water S_w % at ambient conditions and different pH by the cross linked PVA with different mol % EDTA.

	PVA-10mol%EDTA				**PVA-20mol%EDTA**				**PVA-30mol%EDTA**			
Time(h)	pH4	pH5	pH6	pH7	pH4	pH5	pH6	pH7	pH4	pH5	pH6	pH7
2	132.2	138	149	154.3	111.3	116.1	120.2	125	102.2	107	111.1	116.5
4	144.3	149.2	158.2	163.2	119.4	122.2	124.5	127.2	108.8	109.2	116.1	122.3
6	148.1	156	160	167	123.4	125.2	127.6	131.2	114	117	120.8	122.2
8	153.2	162.1	164	172.4	127.8	129	131.5	135.2	120.5	121.2	123.6	126.6
10	154.5	163	164.8	173	129.5	131.2	134.8	138.6	121	122.4	124.8	127.5
24	154.5	163	164.8	173	129.5	131.2	134.8	138.6	121	122.4	124.8	127.5

Table (4) : Water S_w% at ambient conditions and different pH by the cross linked PVA with a mixture of 20 mol% MA/5 mol% EDTA and a mixture of 20 mol% MA/10 mol% EDTA.

Time(h)	**PVA-20 mol% MA/5 mol% EDTA**				**PVA-20 mol% MA/10 mol% EDTA**			
	pH4	pH5	pH6	pH7	pH4	pH5	pH6	pH7
2	106.2	111.4	116.2	119.5	103.4	106.2	110.1	115
4	110.1	114.5	119	121.2	102.2	109.8	112.4	118
6	115.2	117.3	121.2	123.2	104.2	122.2	115.8	120.2
8	117.1	120	122.2	125.1	106.1	113.6	118.2	122.1
10	117.9	120.4	122.5	125.8	106.8	114.1	119.4	123.2
24	117.9	120.9	122.5	125.8	106.8	114.1	119.4	123.2

Table (5): Maximum water S_W% at equilibrium by the cross linked PVA membranes at different pH and ambient conditions.

Sample	pH4	pH5	pH6	pH7
PVA-10 mol% MA	145	149	154.2	162.1
PVA-20 mol% MA	124	125.1	130.6	131.8
PVA-30 mo % MA	118.6	119.7	121.2	121.8
PVA-10 mol% EDTA	154.5	163	164.8	173.1
PVA-20 mol% EDTA	129.5	131.2	134.8	138.6
PVA-30 mo % EDTA	121	122.4	124.8	127.5
PVA-20 mol% MA/ 5 mol% EDTA	117.9	120.4	122.5	125.8
PVA-20 mol% MA/ 10 mol% EDTA	106.8	114.1	119.4	123.2

Table (6):Volume fraction at equilibrium swelling (V_r),average molar mass (Mc), and crosslink density (ρ_c) for the cross linked membranes.

Sample	v_r	$\bar{M}_c$ *10^{-2} (g/mol)	ρ_c *10^4 (mol/g)
PVA-10 mol %MA	0.327	18.64	2.7
PVA-20 mol %MA	0.376	10.57	4.7
PVA-30 mol %MA	0.393	9.01	5.5
PVA-10 mol %EDTA	0.313	22.73	2.2
PVA-20 mol %EDTA	0.362	12.66	3.95
PVA-30 mol %EDTA	0.382	93.02	5.38
PVA-20 mol %MA/5% mol EDTA	0.385	9.62	5.20
PVA-20 mol %MA/10 mol% EDTA	0.395	8.79	5.70

Fig(1): Tensile testing machine

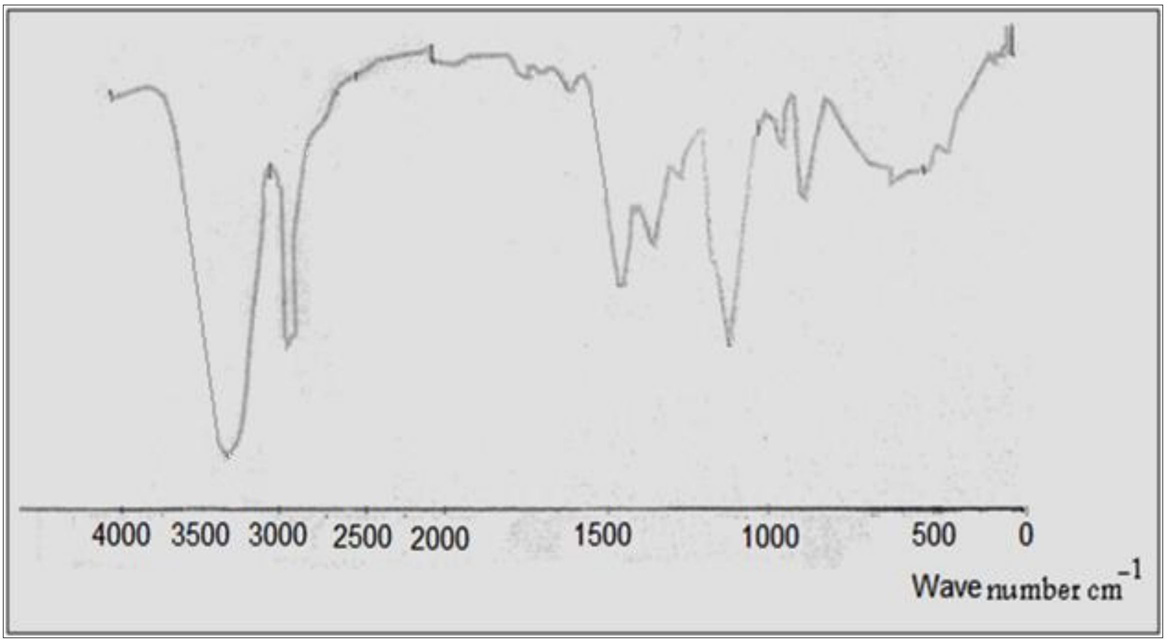
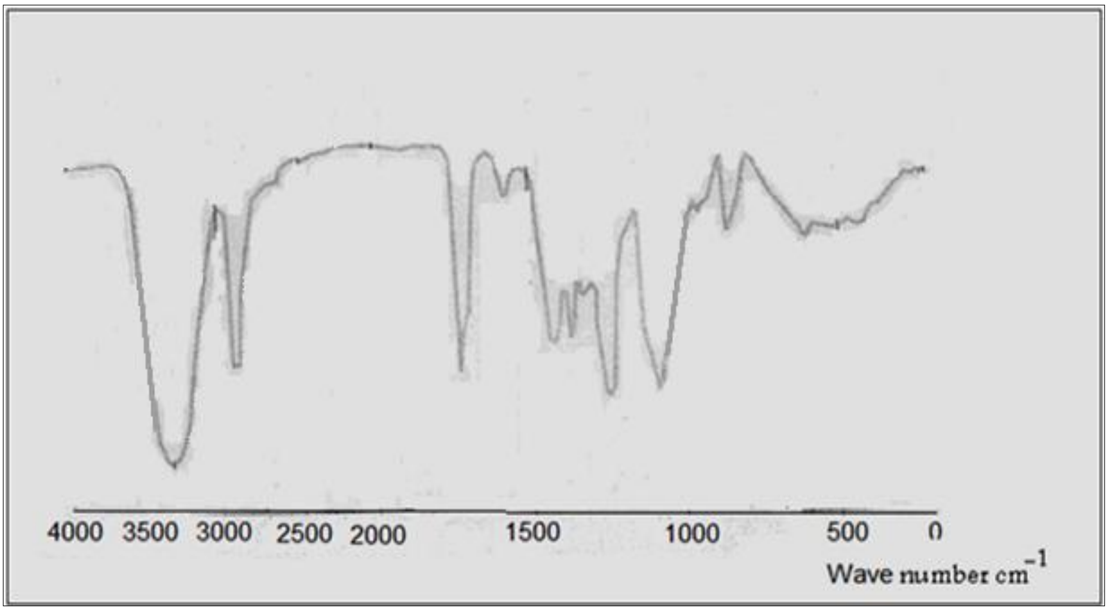


Fig (2): FTIR spectral pattern of PVA



Fig(3): FTIR spectral pattern of PVA-10mol% MA

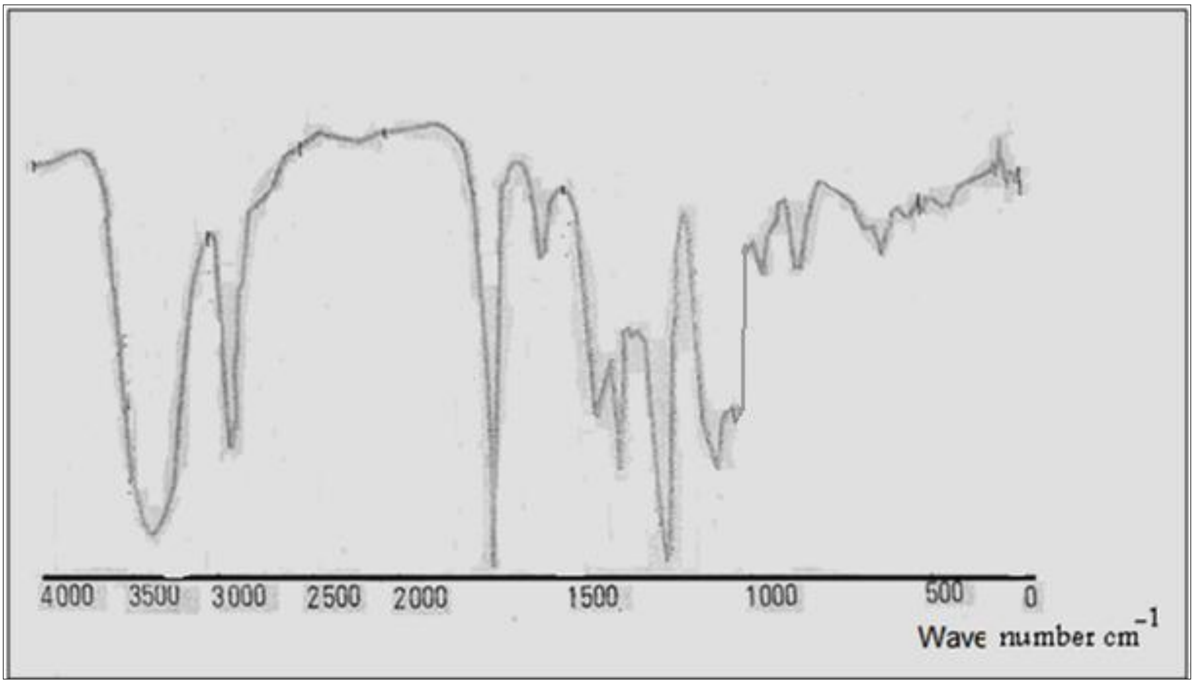


Fig (4): FTIR spectral pattern of PVA-10mol % EDTA

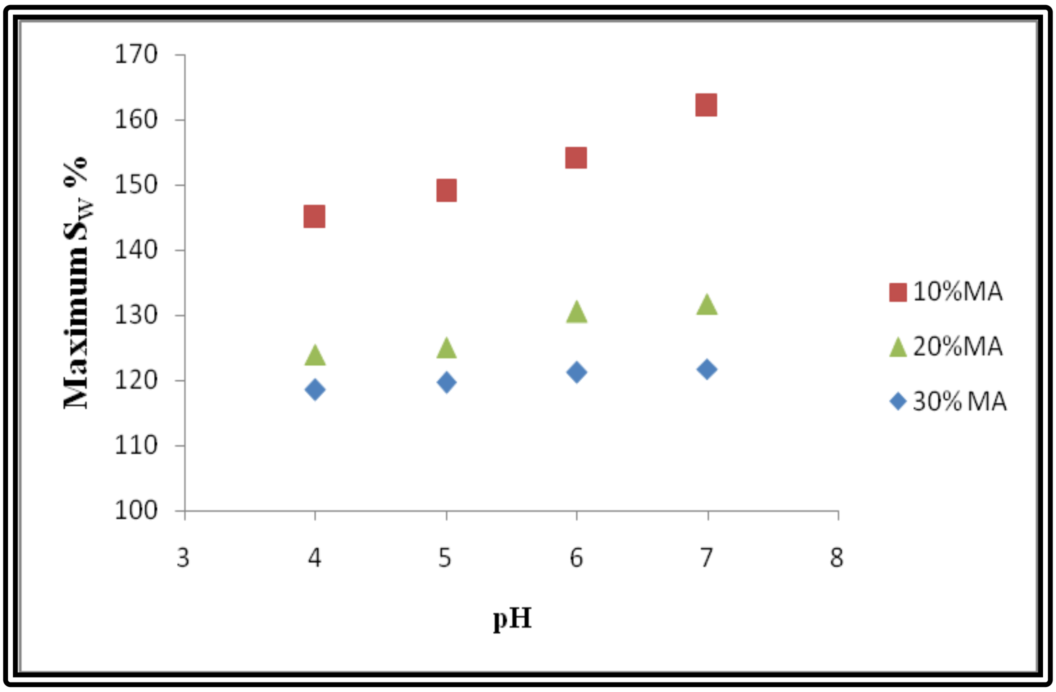


Fig (5): Maximum S_w% of cross linked PVA with different mol% MA at different pH and ambient conditions.

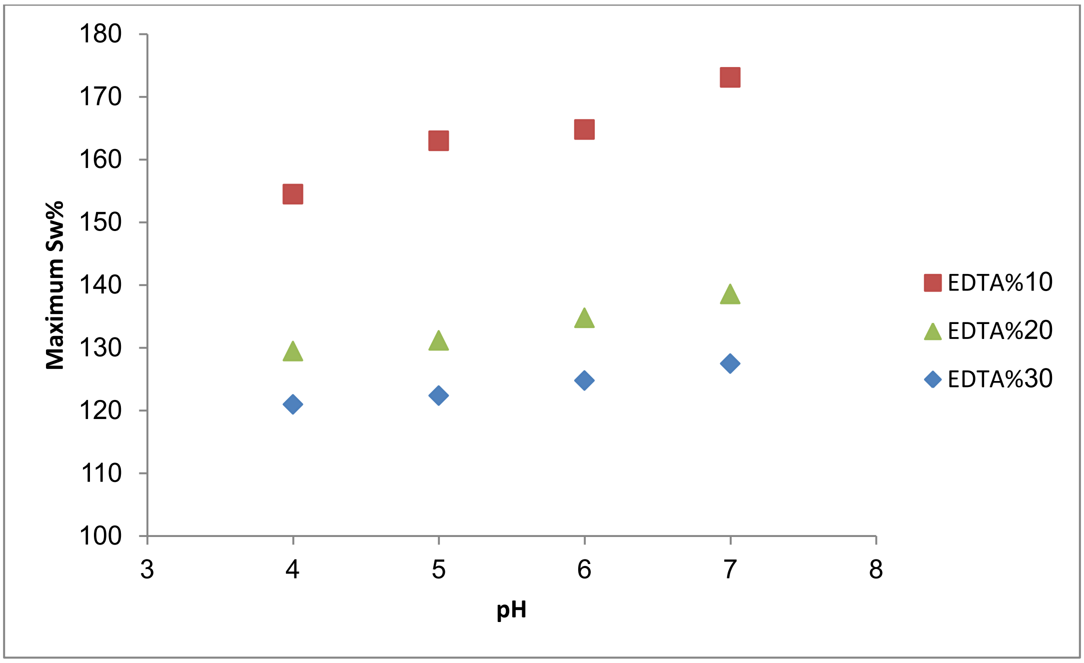


Fig (6): Maximum S_w% of cross linked PVA with different mol% EDTA at different pH

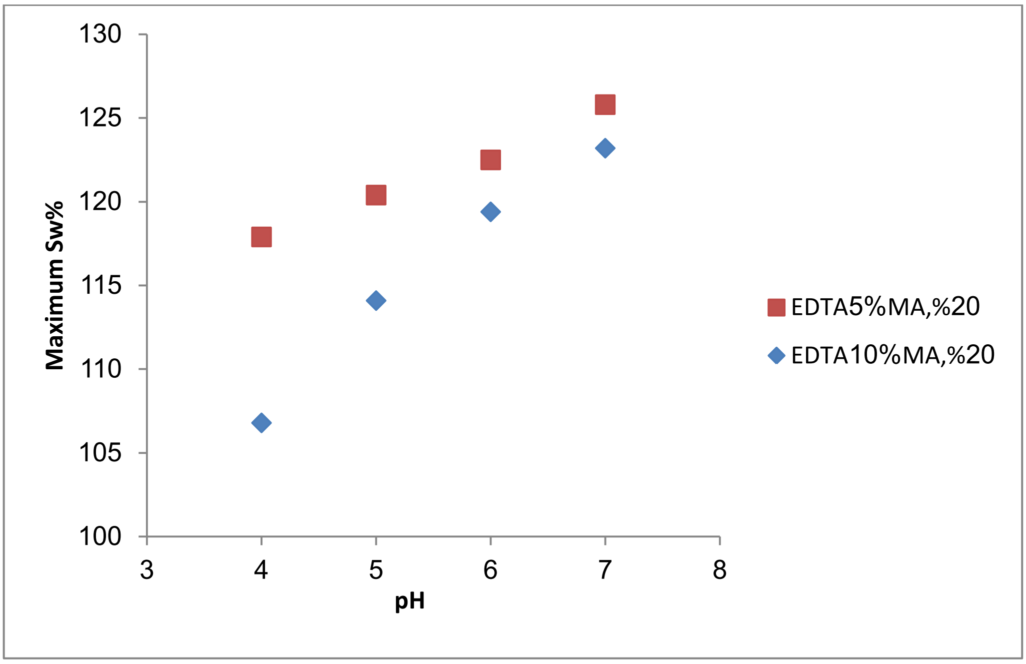


Fig (7) : Maximum water S_w% of cross linked PVA with mol% mixture of MA/EDTA at different pH and ambient conditions.

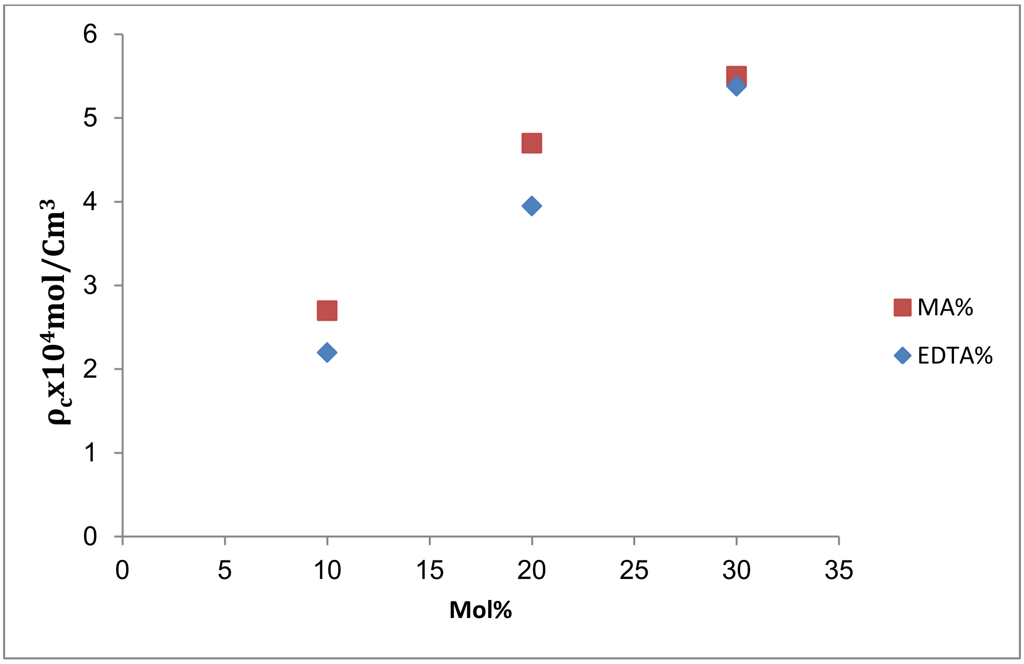


Fig (8) : Cross link density for cross linked PVA with different mol% MA and different mol% EDTA.