

Swelling Behavior of Cross-link PVA with Glutaraldehyde

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Abstract

The polymeric hydrogels composed of poly vinyl alcohol (m.wt 72000) and glutaraldehyde(5%,8% and 10%) , have been thermally prepared for the purpose of studying their swelling and drug release behavior .

The swelling ratio was measured for all the hydrogel samples at 37°C, in three different media pH (1.2, 4.7 and 6.8) as a function of time. The results show that the maximum swelling ratios were arranged as follows :pH =6.8 > pH =4.7 > pH =1.2 hydrogels cross linked PVA showed a typical pH responsive behavior such as high pH has maximum swelling while low pH shows minimum swelling.

Keywords:- Swelling,poly(vinyl alcohol),cross-link polymer,hydrogels.

Introduction

Hydrogels are polymer networks held together by physical or chemical cross-links although the polymer is hydrophilic, the crosslinks make the gel insoluble in water. These networks are stable at room temperature and swell when immersed in water. The extent of the swelling is determined by the density of cross-links and the intrinsic properties of the polymer [1]. The swelling properties, which usually use degree of swelling to define hydrogels, depend on many factors such as network density, solvent nature and polymer solvent interaction parameter [2]. The combination of thermodynamic and elasticity theories states that a cross-linked polymer gel is immersed in a fluid and allowed to reach equilibrium with its surroundings is subject only to two opposing forces: the thermodynamic forces of mixing and the elect active forces of the polymer chains[3]

In aqueous solution, a network of covalently cross-linked polymers imbibes the solution and swells, resulting in a hydrogel. The amount of swelling is affected by mechanical forces, pH, salt, temperature, light and electric field [4]. Three major elements control the swelling process of a hydrogel, The cross-link content, the ionic content and hydrophilic content.

A swellable hydrogel is in its glassy state. When water comes into contact with the hydrogel, swelling will begin as water penetrates between the chains. The process is self-accelerating and a sheath of the "swollen polymer" is formed. Water then travels through the sheath to reach the interior of the hydrogel [5].

Experimental

Chemical

Poly(vinyl alcohol) from Aldrich purity(98%), Glutaraldehyde from BDH purity(99%), Methanol from Aldrich purity(99%), Glacial acetic acid from BDH purity(99%), Sulphuric acid from BDH purity(99%), Buffer solution from Aldrich purity(99%).

Instrument

1. FTIR, Infrared spectra were recorded on shimadzu 8300 fourier transform range(400-400 cm^{-1}) at College of Education for Pure Science/ Ibn Al-Haitham, Baghdad university.
2. Water bath, Dubnoff metabolic shaking incubator .USA.
3. Balance, Sartorius, Germany.

Synthesis of cross-linked of PVA M.wt (72.000)Hydrogel with glutaraldehyde.

A (1.5 gm) of PVA was dissolved in 13.5 gm of hot water at (90 °C), after cooling to room temperature, this solution was mixed in (25 ml) beaker with prepared solution (50% Methanol), 10% glacial acetic acid, 1% sulphuric acid, three different percentages of glutaraldehyde were used as crosslinking agent (5%,8%,10%) in beaker magnetically stirred at room temperature for 6 hours. Then the cross-linked was formed. The reaction mixture was poured into glass mold rectangular shape with dimension 15x5 cm^2 and 0.5 cm height made and used for casting a polymer, left for few days at room temperature, to dryness, a thin film was formed, dried at 40 °C for 14 hours[6].

Swelling

Dried hydrogel pieces were used to determine the swelling ratio (Rs). The Rs was determined by immersing the hydrogel (0.1) gm in 100 ml of different pH (1.2, 4.7, 6.8) and was allowed to soak for 9 days at 37 °C. After every 10 min, they were removed from the water blotted with filter paper to remain surface water and weighted then the (Rs) was calculated :-

$$Rs\% = \frac{ws-wd}{wd} \times 100$$

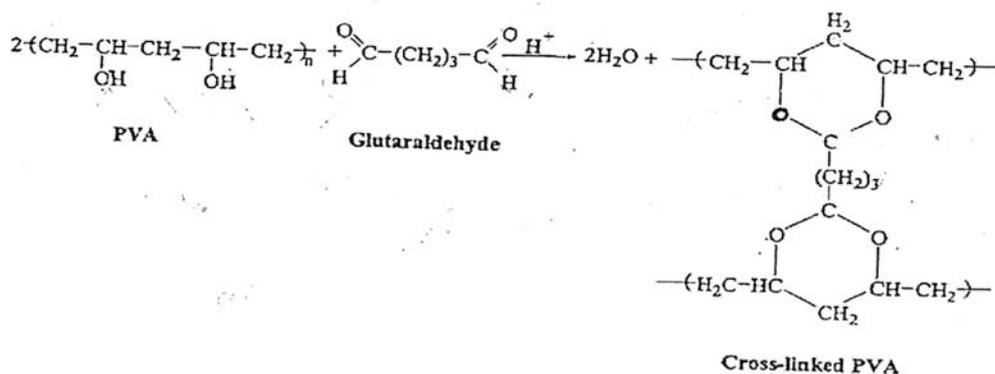
Ws= swollen polymer weight

Wd=dry polymer weight

Result and Discussion:

In this study, a glutaraldehyde was used to crosslink to PVA to evaluate its effect on drug release. Glutaraldehyde reacts with polymers containing hydroxyl groups, such as PVA to form covalently cross-linked networks [7]. The reaction between PVA and glutaraldehyde was characterized by FTIR spectra analysis.

The products of reaction of PVA with aldehydes are poly (vinyl acetal) resins [8]. The gelation of PVA by dialdehyde (glutaraldehyde) is shown as following scheme (3.1).



cross-linked PVA with GA

Characterization of the PVA hydrogels by FTIR.

Fig. (3.1) shows FTIR spectrum of pure PVA sample. It clearly reveals the major peaks associated with PVA. For instance, it can be observed C-H broad alkyl stretching band ($\nu = 2820-2941 \text{ cm}^{-1}$) ($\nu = 3267-3329 \text{ cm}^{-1}$) intermolecular and intermolecular hydrogen bonding are expected to occur among PVA chains due to high hydrophilic forces. An important absorption peak was verified at ($\nu = 1086 \text{ cm}^{-1}$).

This band has been used as an assessment tool of PVA structure because it is a semi crystalline synthetic polymer able to form some domains depending on several process parameters [9].

Fig. (3.2) shows FTIR spectrum associated with PVA cross-linked by glutaraldehyde (PVA/ GA) it can be observed that two peaks at $\nu = 2870$ and 2746 cm^{-1} of C-H stretching are related to aldehydes, a duplet absorption with peaks attributed to the alkyl chain [10]. By crosslinking PVA with GA, the O-H stretching vibration peak $\nu = 3386-3392 \text{ cm}^{-1}$ was decreased when compared to pure PVA fig (3.1)

This result suggests that the hydrogen bonding becomes weaker in cross-linked PVA than in pure PVA because of the diminution in the number of O-H groups and acetal formation. The relative increase of the (C=O) band at approximately $\nu = 1716 \text{ cm}^{-1}$ indicates that the aldehyde group of GA did not completely react with O-H groups of PVA chain. In addition the C-O stretching at approximately $\nu = 1085 \text{ cm}^{-1}$ in pure PVA is replaced by a broader absorption band $\nu = 1089 \text{ cm}^{-1}$ which can be attributed to ether (C-O) and the acetal ring (C-O-C) bands formed by the crosslinking reaction of PVA with GA. Therefore, it can be assumed that it has acted as chemical cross linker among PVA.

Effect of crosslinking ratios on the swelling

The effect of different ratios of GA / PVA was studied on the swelling characteristics of the PVA hydrogel. The effect of cross-linking concentration on the swelling properties of PVA hydrogel is shown in Figures (3,4) to (3.6). As this figure indicates different ratios of GA / PVA show significant difference in their water uptake qualities $P < 0.05$ change entanglement a long with increase in cross-linking agent concentration would result in a decreased network expansion lower GA /PVA ratio cause a significant increase in swelling properties $P < 0.05$. In general, it may be concluded that by increase in the GA /PVA ratio, the cross-linking density increases and this in turn reduces the swelling or water uptake of the gels significantly.

In the hydrogel synthesis, crosslinking agent prevent dissolution of the hydrogels. GA act as cross linker. Higher cross linker concentration decreases the space between copolymer chains and, consequently, the resulted highly cross linked rigid structure cannot be expanded and it holds a large quantity of water [11].

Figures (3.4) to (3.6) show difference in swelling at equilibrium at different ratios of GA 5%, 8%, 10% of cross-linked PVA in buffer solution 6.8, 4.7, 1.2

The swelling ratios of all formulations in HCL solution of pH 1.2, 4.7, 6.8 were found to be increased with time. The swelling ratios of super porous hydrogel decreased by increase in the crosslinking density, as much tighter networks were formed higher consent. Ratio of crosslinking agents. The amount of crosslinking agent had influence on the swelling ratio of the polymer and assist concentration increased, polymer chain was attached to each other more strongly and the size of pores during foam formation was smaller [12,13]. In prepared hydrogel pH dependent swelling was observed that could be attributed to ionizable functional groups. PVA contain high hydroxyl groups that make this polymer high interactive with water. The glutaraldehyde content increasos, the extent of crosslinking increasos and consequently the % equilibrium swelling decreasos [14].

Effect of pH on the Swelling:

Figures (3.10) to (3.12) show PH –sensitive characteristics of hydrogels, which are investigated by swelling test under various pH ranges 1.2, 4.7, 6.8. In the swelling kinetics of PVA/ GA hydrogels, all PVA/ GA hydrogels reached an equilibrium after about 20 min. The water content increased with pH of buffer solution. At pH 6.8, the water content drastically increased due to the hydrogel. Thus, the ionic repulsion caused by formation of carboxylation, donated the swelling behavior.

Figures (3.10) to (3.12) show the difference in swelling at equilibrium at pH 1.2, 4.7, 6.8 at 37 °C for cross-linked PVA hydrogels prepared with varying degree of GA.

Conclusions:

- 1- Modification of PVA membrane by thermally crosslinking with different ratios (5% , 8% and 10%) GA and PAA
- 2- FTIR spectroscopy indicates the formation of cross-links hydroxyl groups of PVA and functional group of crosslinking agents .The type of crosslinking agent and the crosslinking density are important factors determining the pH –sensitive swelling behavior .
- 3- The swelling of PVA/GA hydrogels can be well explained by fiction swelling equilibrium .
- 4- Swelling ratio is affected by the amount of crosslinking agent , the results show highly cross linked hydrogel causes a significant decrease in swelling properties .
- 5- Hydrogels showed a typical pH responsive behavior at 37 °C ,as high pH had maximum swelling as follows
pH =1.2 < pH =4.7 < pH =6.8

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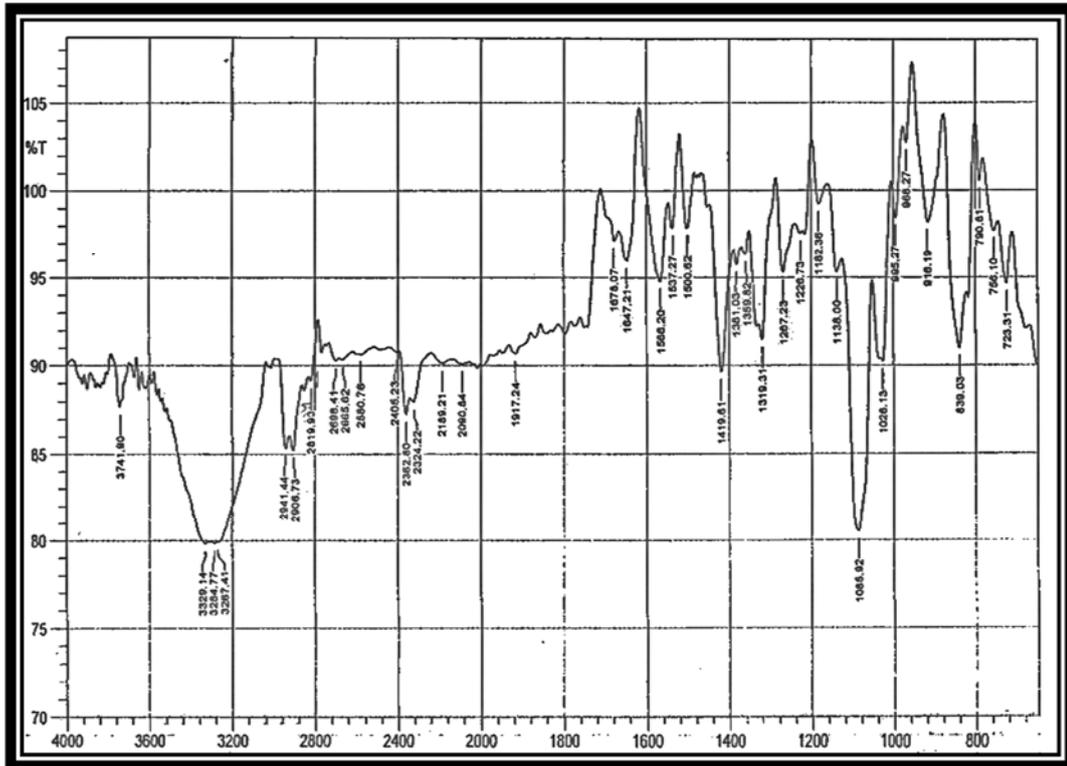


Figure No. (1): FTIR spectra for puer PVA

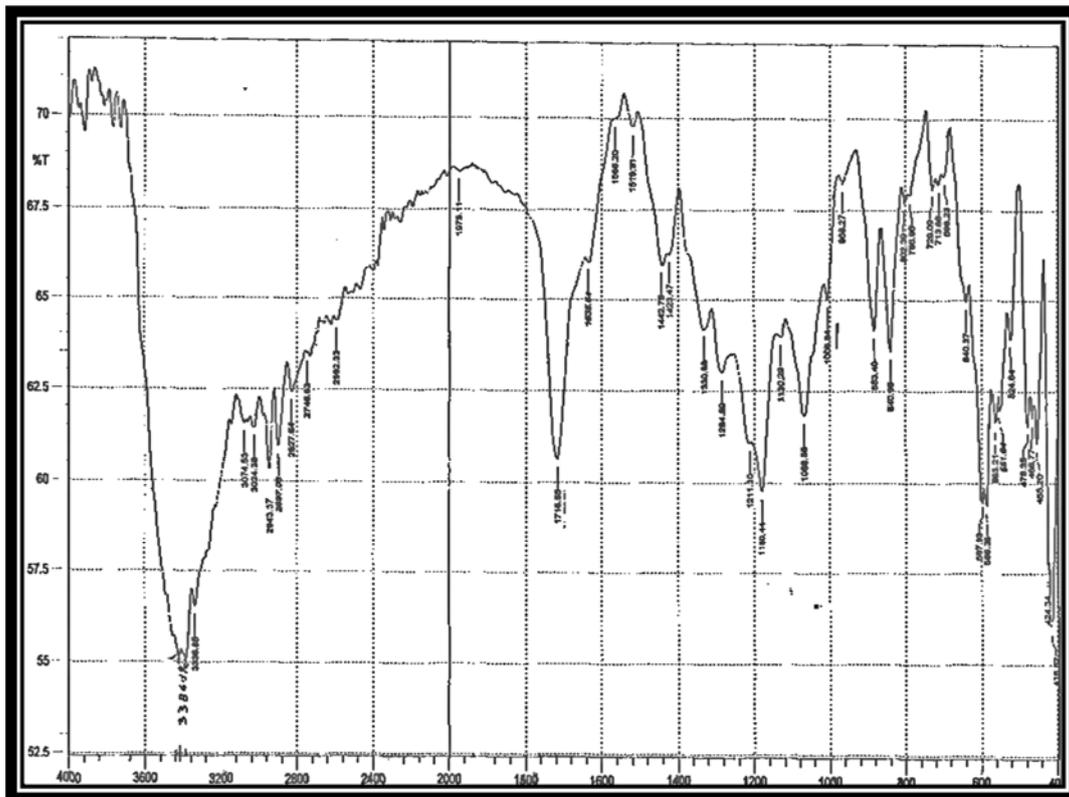


Figure No. (2): FTIR Spectra of cross-linking (PVA)

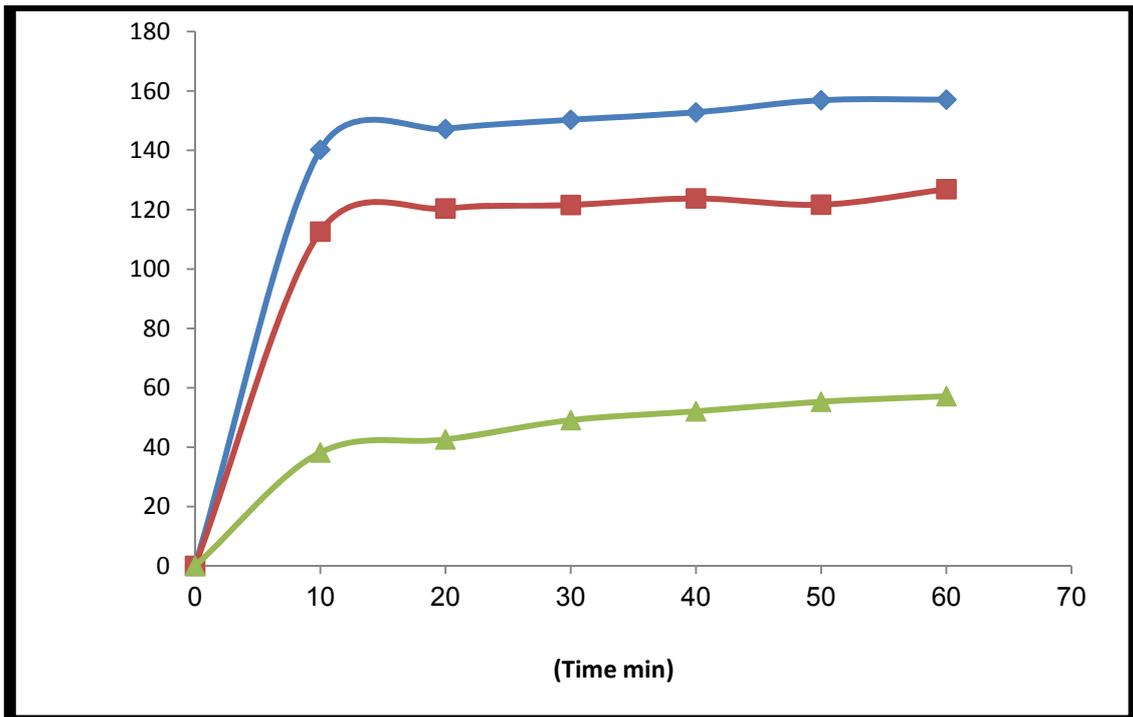


Figure No.(3): Effect of different ratios of (GA/PVA) on the swelling of PVA hydrogel in PH6.8 at 37°C

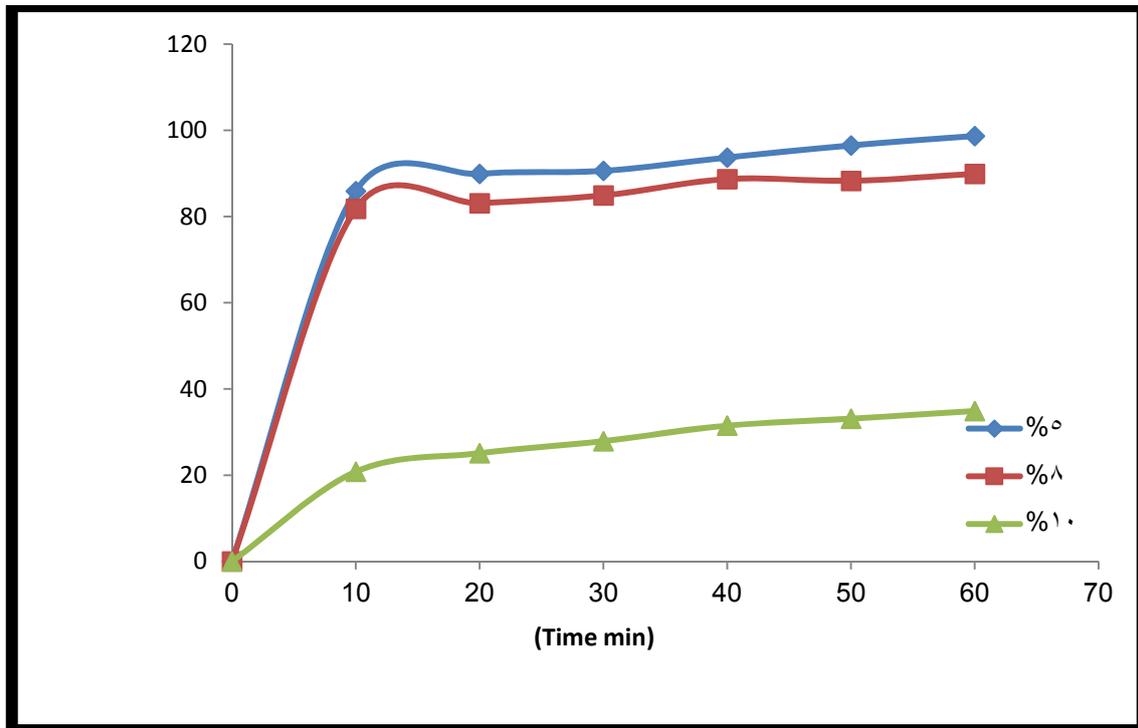


Figure No. (4) :Effect of different ratios of (GA/PVA) on the swelling of PVA hydrogel in pH 4.7 at 37°C

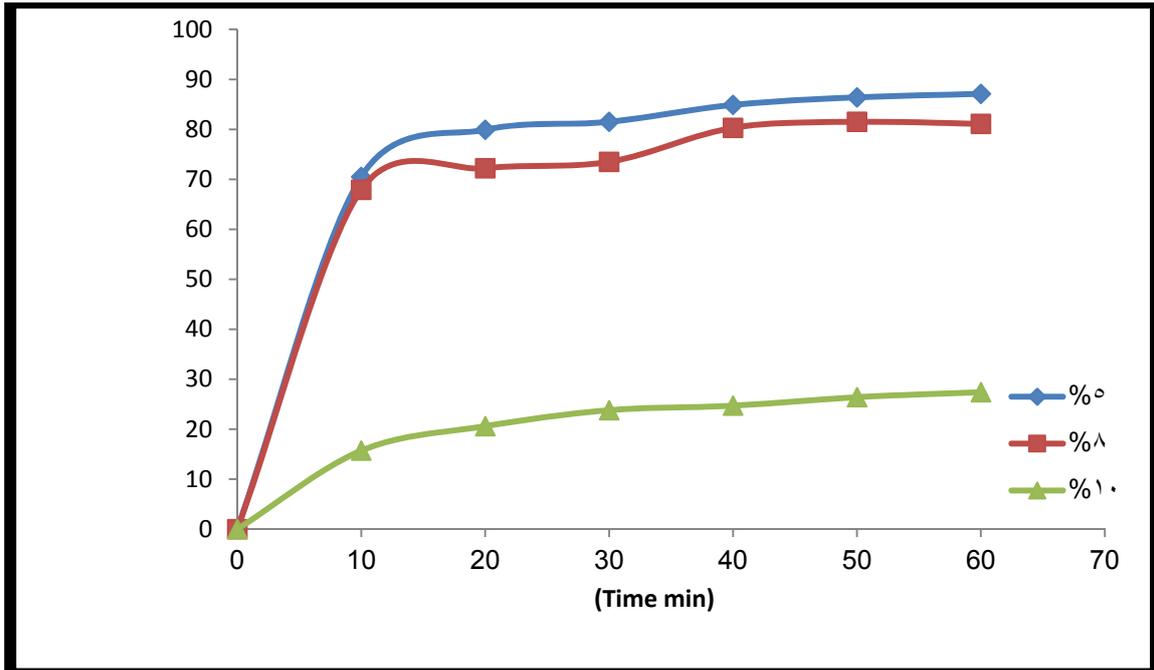


Figure No.(5): Effect of different ratios of (GA/PVA) on the swelling of PVA hydrogel in pH 1.2 at 37 °C

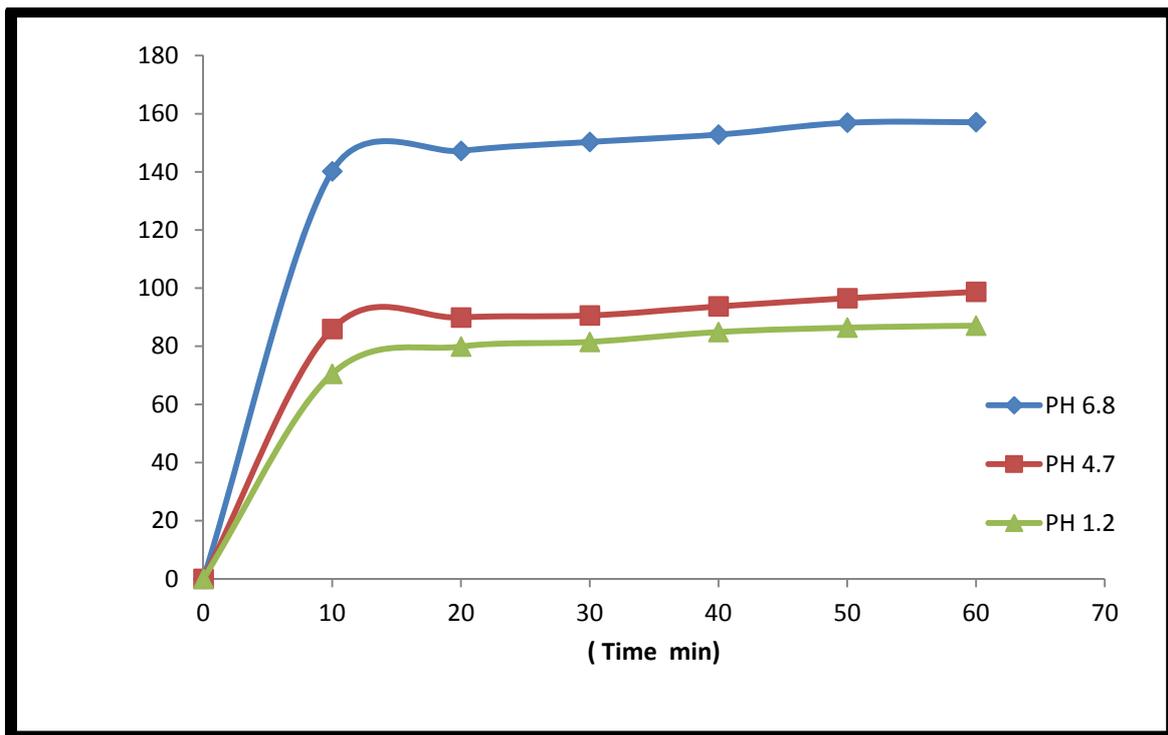


Figure No. (6) : Swelling of 5% (PVA/GA) hydrogels at various pHs (at 37 °C)

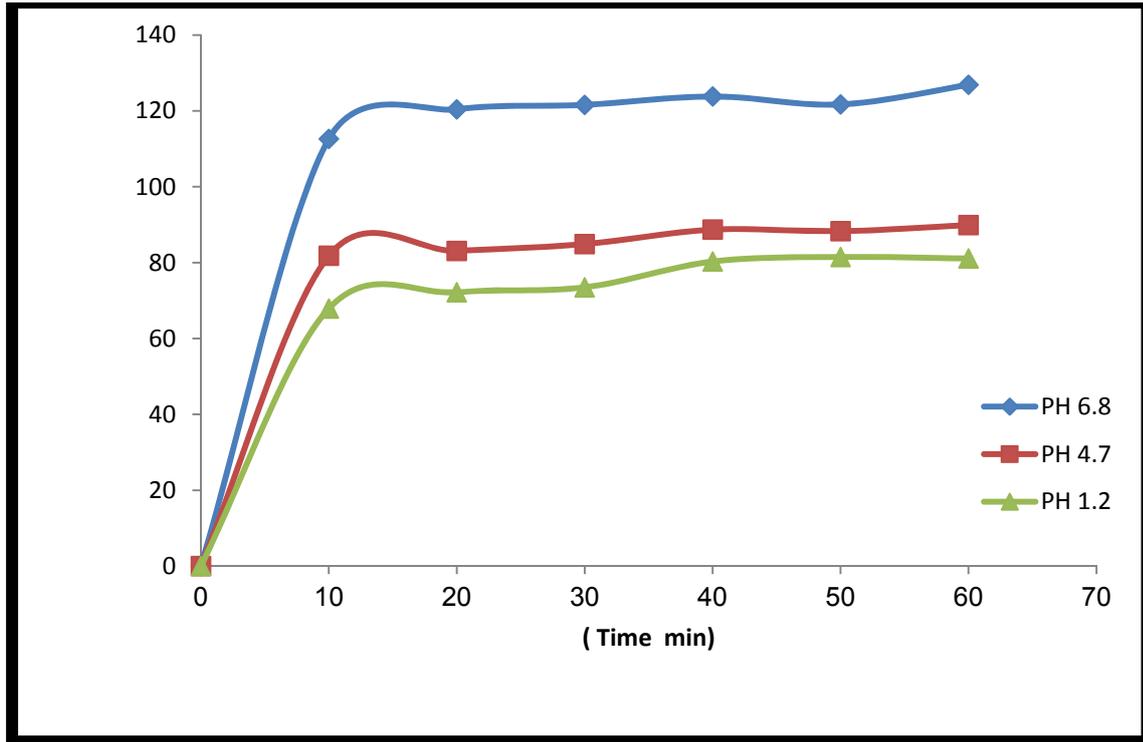


Figure No. (7): Swelling of 8% (PVA/GA) hydrogels at various pHs (at 37 °C)

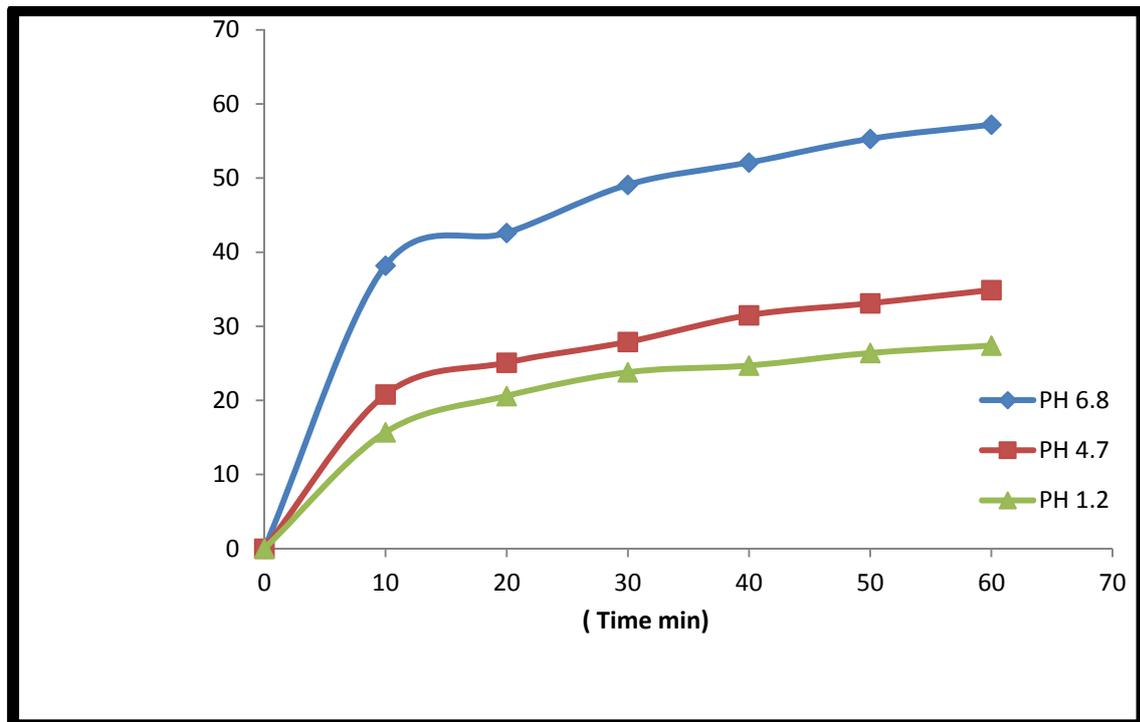


Figure No. (8): Swelling of 10% (PVA/GA) at various pHs (at 37 °C)

سلوك الانتفاخ للبولي فاينيل الكحول المتشابك عرضيا مع الكلوتارالديهيد

فاضل سليم متي

مها ظاهر سلطان

أديبة خيون أمين

قسم الكيمياء /كلية التربية للعلوم الصرفة (ابن الهيثم) /جامعة بغداد
استلم البحث في: ٢٩ أيار ٢٠١٥ ، قبل البحث في: ٢٦ نيسان ٢٠١٥

الخلاصة

ان البوليمرات الهلامية متراكبة من بولي فاينيل الكحول وكلوتارالديهيد حضرت حرارياً لغرض دراسة ظاهرة الانتفاخ. النماذج المحضرة تختلف بالعوامل المستعملة في التشابك ونسب التشابك كآلاتي .

PVA (M.wt 72000) +GA, 5% , 8% and 10%)

ان التركيب الكيميائي ل PVA المتشابك الهلامي وال PVA الخطي تم تشخيصه بوساطة طيف FTIR اذ اثبتت النتائج تكون تشابكات بين مجاميع الهيدروكسيل ل PVA والمجاميع الفعالة لعوامل التشابك. وقد تم قياس نسب الانتفاخ لجميع نماذج الهلامية عند درجة 37°C في ثلاثة اوساط مختلفة ال pH التي هي (1.2 , 4.7 , 6.8) كدالة للزمن.

وتم ملاحظة ان درجة الانتفاخ لهلاميات PVA المتشابكة تعتمد على قيمة pH لمحاليل بفر. وتم دراسة تأثير قيمة pH في نسب الانتفاخ لجميع التراكيب الهلامية ووجد من النتائج ان اعلى نسبة انتفاخ كانت حسب الترتيب الاتي .

$\text{pH} = 6.8 > \text{pH} = 4.7 > \text{pH} = 1.2$

الكلمات المفتاحية: سلوك الانتفاخ، بولي فاينيل الكحول، البوليمرات المتشابكة عرضيا، الجيل