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Effect of Graft Ratio PVA-Urea and Different Concentration Blend Polymers on Swelling Ratio

Abbas Khamas Hussein Bassam Ibrahim Khalil* Hind Hussein Abud
Department of Materials Engineering, University of Technology, Baghdad-Iraq

Abstract

The polymeric materials still important parameters for drug delivery research.In the present work two graft polymers PVA-U were prepared from reaction polyvinyl alcohol PVA and urea by using two ratio concentration from urea. Were blending 8% PVA-U and 5% Hydroxypropyl methylcellulose HPMC in different ratio 100:0, 75:25 and 50:50 with using glutaraldehyde as crosslinked agent 0.75 ml/dl. The structure of PVA-U and blend PVA-U/HPMC hydrogel was characterized by Fourier transform infrared spectroscopy FTIR, differential scanning colorimeter DSC and scanning electron microscopy SEM. Studies are made on swelling behavior for all prepared samples in different media of PH (neutral, acidic and alkaline) and deionised water.. It is found that swelling ratio depends on media and proportion of substitutes in graft polymers, in high graft polyvinyl alcohol the swelling ratio increased with pH increased from pH2 < dionized water ≤ PH7 < PH10, But in low graft polyvinyl alcohol the swelling ratio increased with pH increased from pH2 < PH10 < dionized water ≤ PH7. Swelling ratio of polymeric hydrogels was affected by composition blend polymers and it was increased by increasing the concentration of HPMC and decrease time for complete swelling.

Keywords: Blend polymers, Hydrogel polymers, PVA, HPMC, Glutaraldehyde

1. Introduction

Hydrogels are defined as polymer materials that are polymeric hydrophilic network of three dimensional crosslinked structures and these hydrophilic polymeric networks capable of imbibing large amount of biological fluids or water and thereby swell. The ability of polymer hydrogels to absorb water and biological fluid is due to the presence of hydrophilic groups such as hydroxyl groups -OH, carboxyl groups -COOH, amino groups -NH3, sulphonic -SO3H.... etc. Thus, crosslinked polymeric network which has the capacity to hold water within its porous structure and hydrogels can uptake water nearly 10-20 times its molecular weight and swelling without the polymer dissolving (Distantina, & Rochmadi, 2012 ; Chauhan *et al.* 2012). Mostly water-soluble polymers have been used as reagents that would undergo chemical or physical cross linking processes. Cross linked PVA hydrogels are useful in sustaining drug release and good swelling property too. Chemical cross linking generally results in modified and improved polymer properties such as physical, mechanical, thermal and chemical stability. Polyvinyl alcohol based hydrogels have limited applications due to poor mechanical strength. Polymers blending are a simple yet attractive method to overcome this limiting factor and it provides improved chemical and physical properties to the hydrogels. Crosslinking and grafting are the two methods commonly employed to improve and modify the functional properties of the hydrogels (Marten 1968; Gibas & Helena 2010 ; Gajra *et al.2012*)

There are crosslinking agents have di-functional groups used for the crosslinking of PVA like: acetaldehyde, gluteraldehyde, epichlorohydrin, formaldehyde and other. With the crosslinking agents there must be presence of sulfuric acid, methanol or acetic acid to form the acetal bridges between the hydroxyl groups of PVA chains (Ratha & Arnab 2012; Hossein 2013)

Hydroxypropyl methylcellulose (HPMC), commonly known as hypromellose also, is preparation from modification of the naturally occurring cellulose and is considered safe for normal consumption in humans. Hydroxyl propylmethylcellulose (HPMC) has been one of the most widely studied polymers in the last years. The reason for its widespread acceptance because of solubility characteristics of Hydroxypropyl methylcellulose in gastrointestinal fluid, in organic and aqueous solvent systems, non interference with drug availability and tablet disintegration, absence of taste and odor, flexibility and chip resistance, stability in the presence of light, air, heat and reasonable levels of moisture, ability to incorporate color and other additives into the film without difficulty. (Al-Tabakha 2010; Fatimi et al.2009; Ghosal et al.2011).

2. Materials and Methods:

2.1 Materials

Polyvinyl alcohol (PVA) (M.W. ~ 72,000), was obtained from Fluka, U.K . Urea, purity 99.8% was obtained from Aldrich Chemical Co. Inc. (UK). Dimethyl sulfoxide (DMSO) from *Sinopharm Chemical Reagent Co.,Ltd.* Ethanol, purity 95%was obtained from Tomas Baker- India. Hydroxypropyl methylcellulose (HPMC) from Aldrich Chemical Co. Inc. (UK). Glutaraldehyde (GA) 25 % from Sigma-Aldrich. Sulfuric acid purity 95% was obtained from Fluka. Different buffer solutions of pH 2, 7 and 10 were prepared.

2.2 Preparation of graft polymer:

Preparation of graft polymer polyvinyl alcohol (U-PVA) this was prepared according to literature method (Al.Jeboore et al. 2010), by reaction (PVA) with urea as follows: (250 ml) two-necked flat bottomed flask, equipped with a condenser, thermometer and a magnetic stirrer, Afterwards the flasks are equipped with the materials and reagents PVA 10 gm , Urea (13.6 gm or 6.8 gm) and 50 ml DMSO in the different ratio for prepare two different samples from graft polymers as described in the table (1), Thereafter, allowed to the contents of the flask are heated under reflux for three hours. The stirred mixture was allowed to cool to room temperature, and by adding Ethanol, and then dried figure (1).

2.3 Synthesis Hydrogels:

2.3.1 Preparation of Polyvinyl Alcohol-Urea Solutions:

Graft polymer urethanised (U-PVA) 8% was prepared by dissolved 8 gm PVA-U (A) in 100 ml deionized water at room temperature with continuous mechanical stirring until clear solution. The same way to prepare solutions of compounds (B).

2.3.2 Preparation of HPMC Solutions:

Hydroxypropylmethylcellulose (HPMC) 5% was prepared by dissolved 5 gm HPMC in 100 ml deionized water at room temperature with continuous mechanical stirring until clear.

2.3.3 Preparation of Crosslinking U-PVA with HPMC

The hydrogels were prepared mixing various types from 8% (U-PVA) solution, 5% HPMC solution, 25% glutaraldehyde and 10% Sulfuric acid are shown in table (2). The mixture PVA-U solution and HPMC solution was stirred constantly until uniform and the crosslinking agent and sulfuric acid were added into the mixture under constant stirring about 30 min and 50 ^{0}C . After well mixing, the mixture was poured into a plate 24 wells and the gel formed within 30 minutes. The hydrogels product was dried room temperature overnight shown in figure (2).

2.4 Characterization

Infrared spectrum of prepared specimens was obtained in absorption in the range of 400 – 4000 cm-1 by using FTIR type is (TENSOR-27), made by (Bruker Optics Company). The test is performed according to (ASTM E1252) (ASTM Standard2013). Differential Scanning Calorimetric (DSC) Analysis was performed using (LINSEIS Company-USA), type is (DSC PT1000). DSC tests were carried out according to (ASTM D3418) to measure the changes in physical properties that taking place in the test samples, particularly the glass transition temperature. All analysis were carried out on samples have mass (10 mg),at differential scanning calorimetric programmed between 25^{o}C to 400^{o}C with heating rate of specimen (10^{o}C /min). The glass transition temperatures (Tg), the crystalline temperatures (Tc) and melting temperatures (Tm) of the samples were determined from the DSC spectra as a function of temperature (ASTM Standard2013).

The surface morphology of the surface of graft polymers and hydrogel polymers specimens are cutting at fracture surface, which are analyzed by using scanning electron microscope (SEM), model (AIS2300C), made Seron Technologies Inc. in Korea. The specimens used in scanning electron microscope was cut into dimensions (0.5 cm x 0.5 cm x 0.5 cm) to fit into the device. The fracture surface was observed at different magnifications. To achieve a good electrical conductivity, all specimens are first sputtered with gold from the surface along the edge. Then, secondary electron images are record; with working voltage is kept at (10 Kv) (Qahtan.2015).

2.5 Swelling Study:

The swelling behavior of specimens polymer hydrogels was measured swelling in different pH solutions (PH2, PH7, PH10 and deionised water) at 37 ^{o}C. Hydrogels were dried in vacuum oven for 24 hrs at 50∘C. The dried hydrogel disc of (Approx. 10mg) was immersed in 50 ml (PH2, PH7, PH10 and deionised water) at 37 ± 0.2∘C in an incubator. The swollen discs were withdrawn from the solutions at different time intervals and their wet weight were determined after first blotting with a filter paper followed by blowing with a stream of air to remove the surface water and immediately weighing Swollen discs by using the equation weighed. The percentage swelling ratio was calculated using the following equation (1)

$$E_{sr}\,(\%) = ((Ws - W_d\,) \,/\, W_d\,) \times 100$$

Where Esr% is the percentage swelling ratio. Ws is the weight of the samples in the swollen states at time t. Wd is the initial weight of the samples in the dry states (Abdeen, 2011),(Rohindra, et al.2004).

3. Results and discussion

Polyvinyl alcohol-Urea were prepared from reaction polyvinyl alcohol with urea, the reaction can are shown in figure (3). Figure (4) showed the FTIR spectra of film pure PVA and A and B for pure PVA showed the absorption peaks of PVA occur at 3260 cm^{-1} stretching of -OH and at about 2920 cm^{-1} for the asymmetric stretching of -CH2 , 2852 cm^{-1} for symmetric stretching of -CH_2 . The peak at 1710 cm^{-1} stretching of C=O at acetate groups for degree of hydrolysis PVA and the band at 1659 cm^{-1}at HOH bending is due to deformation vibration of the absorbed water molecules. The peak at 1415 cm^{-1} for the wagging of -CH_2 and bending of OH and the peak at 1086 cm^{-1} for stretching of -CO and bending of -OH from amorphous sequence of PVA, 916 cm^{-1} for at bending of CH_2 and for at 831cm^{-1} rocking of CH (Wang, et al.2004). Curve(4-A and B) Showed the FTIR spectrum of the PVA-U derivatives (A and B) respectively, The PVA-U show spectral features different to that for the pure PVA , because of reaction PVA with urea and the changes in their relative intensity and peak position, Major changes occur in appearing at 3260 cm^{-1} for pure PVA it are shift to between (3330 -3340 cm^{-1}) for N-H stretch amines . appearance peak at 1698 cm^{-1} at -C=O stretch for carbonyls groups in PVA-U due to urea structure and appearance peak at 1620 cm^{-1} at N-H bend for amines groups in PVA-U . The peak at 1090 cm^{-1} for C-N stretch for aliphatic amines and 1012 cm^{-1} for N-H wag for amines. The absorption bands position changes and the peaks become a broad and more intensity in PVA-U compared with pure PVA. Fig. (5) shows the FTIR spectra of 75/25, 50/50, 25/75 (wt/wt) PVA/HPMC blends for (A2) (A3) and (A4). The interactions between the polymer pair in the blending form through functional groups with GA as crosslinked agent, Since these two polymers possess some similar functional groups such as -OH , therefore the group regions of FTIR spectra are partially the same and their spectra differ only in the finger print regions. The blends comprising both components show spectra with characteristic of both but the vibration bands characterizing each polymer are predominating as its content increases. It can be observed that the O-H stretching vibration peak a (3335 cm-1) was decreased when increase ratio HPMC more than pure PVA-U. This is because of the diminution in the number of OH groups in HPMC compare with PVA-U. In addition, the N-H bend at approximately 1699 cm-1 and anther amines groups in the (PVA-U) was increased when increase ratio PVA-U (Ruvalcaba et al.2009). Figure (6) illustrates the general equation preparation of preparation polymer hydrogels derivatives. There are numerous hydroxyl groups and amino groups available on the polymer chains of PVA-U and HPMC that may react with glutaraldehyde. As a consequence, the crosslinked hydrogel materials obtained have a complex structure.

Differential scanning calorimetry (DSC) technique provides information such as glass transition temperature (Tg), melting temperature (Tm) and crystallization temperature (Tc), in addition to the associated enthalpy for each process. The glass transition temperature was taken at the onset of the heat capacity and the melting point at the maximum of the endothermic peak. We found in pure PVA two endothermic peaks, the first peak at 78˚C may be due to a glass transition and a sharp endothermic melting transition at 178˚C as shown in figure (7), the value of Tg and Tm which has been obtained for PVA, is nearly in agreement with that reported previously in the literatures Tg (75-85) and Tm (175-200) (Bianchi, et al.2011). The figure (8) DSC curve of polymer (B) is shown Tg (92 ^{O}C),Tc (155 ^{O}C), Tm (190 ^{O}C) and Td (220 ^{O}C), As it can be seen, Tg was 83^{O}C, Tc (145 ^{O}C), Tm (180 ^{O}C) and Td (217 ^{O}C) for polymer (A) in figure (9). When we compared the curves of polymer (B) and (A) with pure PVA we saw increasing in all the measurements due to the addition of new functional groups of amine groups (-NH2) with varying proportions this is because that the different substituted groups influence in the geometry and polarizability of the molecules that determined the phase and type transition temperatures of the polymer. Polymers having hydrophilic groups such as amide or hydroxyl groups form intermolecular bond which strongly affect the characteristics of the glass transition (Juman,2016)

The changes in surface morphology for the prepared polymer hydrogels was studied by using SEM micrographs. Figure (10) illustrates the surface morphology of sample B1, It can be seen the pure B with Glutaraldehyde as crossliked agent , SEM photos show the pores. The Figure (11) and (12) shows the micrograph of the surface of test specimens of polymers blends of PVA-U and HPMC, with a composition of B3 (50/50) and B4 (25/75), respectively. The observation of domains involving HPMC and PVA-U is clear, and indicates the immiscibility of the blend. The interface compatibility between the HPMC and PVA-U is one of the main factors affecting blend performance.

In the B4 blends are 25/75, with 75% of HPMC as a matrix, and in B3 blends are 50/50 from each polymers, Figures (12) shows increase white zone in continuous phase, whereas other Figure (11) show semi-continuous morphology, the semi-continuous morphology depending on the components of the blend polymers ratio. It was observed that the dispersion of blend polymers was relatively good. The numbers of pores were observed in images of hydrogels increase with increase the HPMC. This increased porosity allows faster water diffusion through the hydrogel network which in turn is another factor that contributes to the higher rate of water uptake observed in hydrolyzed samples.

The chemical structure of polymer chain and repeating unit affect the swelling ratio by affecting the ratio of hydrophilic groups to hydrophobic groups. Polymer hydrogels with hydrophilic groups swell to a higher degree than polymer hydrogels with hydrophobic groups due to the degradation chains minimize their exposure to the water molecule and lower swelling ratio. The swelling properties are due to the presence of hydrophilic groups such as -OH, - $CONH_2$-, CONH- and -SO_3H in the network. The ability of polymer hydrogels to absorb water arises from hydrophilic functional groups attached to the polymers backbone while their resistance to dissolution arises from cross linked between network chains. Water inside the polymer hydrogel allows free diffusion of some solute molecules.

In this study synthesis graft polyvinyl alcohol with high concentration from Urea and low concentration of urea and it was a study the effect ratio of graft polymers on swelling ratio. For graft polymers low concentration Urea the figures from (13) to figures (16) it was show the swelling ratio for (A1 to A4) in different media and. It was observed that swelling ratio increased with increased pH from pH2 < dionized water ≤ PH7 < PH10 due to low concentration amino groups in graft PVA-U compared with hydroxyl groups. For graft polymers high concentration Urea the figures from (17) to figures (20) it was show the swelling ratio for (B1 to B4) in different media. It was observed that swelling ratio increased with increased pH from pH2 < PH10 < dionized water ≤ PH7 due to high concentration amino groups in graft PVA-U compared with hydroxyl groups and the protonation of primary amino groups (NH_3^+) on acidic buffer this lead to decreased swelling ratio with increased PH .

Blends of synthetic polymers and natural polymers represent a new class of composites materials and have attracted much attention especially as biomaterial and bio-application. Although Biological polymers represent good biocompatibility but their mechanical properties are often not good and this causes problems often. Different blends of PVA-U/HPMC hydrogel were prepared as pure PVA-U (A and B), 75/25, 50/50, 75/25 with crosslinked agent. It was observed that there was difference between the swelling percentages of hydrogel in different blend polymers, In general, swelling ratio of blend PVA-U/HPMC increased with increased HPMC ratio.

The amount swelling ratio was dependent on the blend polymer ratio and the swelling ration became higher indicating the role of HPMC amount in increasing the swelling ratio of hydrogels, due to higher hydrophilic nature of the HPMC than the PVA-U and incorporation of hydrophilic HPMC segments along with PVA-U chains into the hydrogels and presence of hydroxyl groups in PVA-U backbone and HPMC. The hydroxyl groups are more hydrophilic from amine groups in PVA-U. The swelling ratio for all blend polymer hydrogels decreased with increased HPMC more than 75% due to the HPMC has more hydrophilic and this lead to increased swelling rate and increased degradation rate. In the other hand, HPMC is biodegreadation more than PVA-U. (Ranjha, et al.2014; Wang & Sundaram 2006)

4. Conclusions

It is found that swelling ratio depends on media and proportion of substitutes in graft polymers, in high graft polyvinyl alcohol the swelling ratio increased with pH increased from pH2 < dionized water ≤ PH7 < PH10, But in low graft polyvinyl alcohol the swelling ratio increased with pH increased from pH2 < PH10 < dionized water ≤ PH7. Swelling ratio of polymeric hydrogels was affected by composition blend polymers and it was increased by increasing the concentration of HPMC and decrease time for complete swelling.

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Table (1): The prepared samples from graft polymers

Code No.	PVA(gm)	Urea (gm)	DMSO (ml)
A	10	6.8	50
B	10	13.6	50

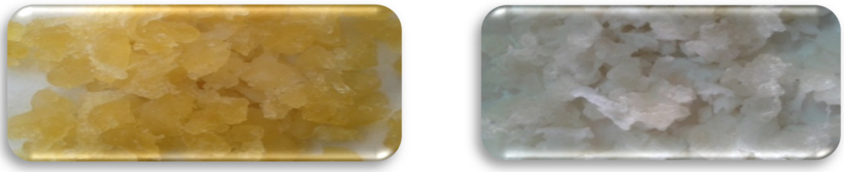

Figure (1): Pattern A shows graft polymer (sample A) with low concentration of Urea
Pattern B shows graft polymer (sample B) with high concentration of Urea

Table (2): Synthesis derivatives hydrogels

NO.	**PVA-U 8% (ml)**	**HPMC 5% (ml)**	**GA25% (ml)**	**Sulfuric acid 10% (ml)**
A1	100	0	0.75	1.0
A2	75	25	0.75	1.0
A3	50	50	0.75	1.0
A4	25	75	0.75	1.0
B1	100	0	0.75	1.0
B2	75	25	0.75	1.0
B3	50	50	0.75	1.0
B4	25	75	0.75	1.0

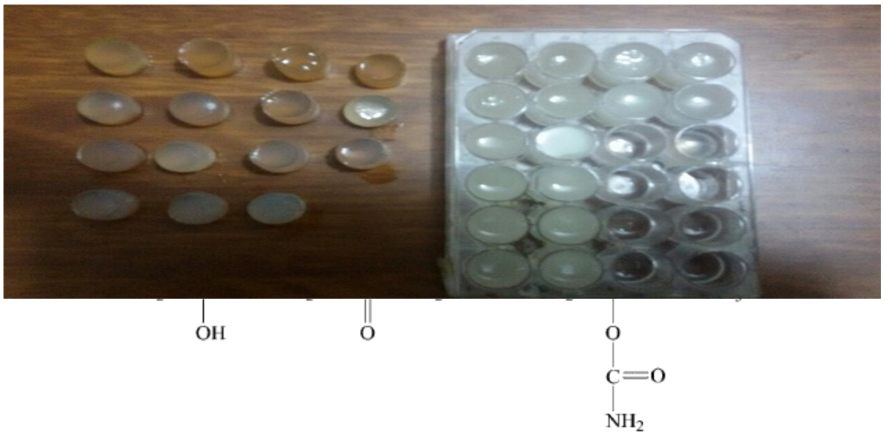

Figure (3): synthesis Polyvinyl alcohol-Urea

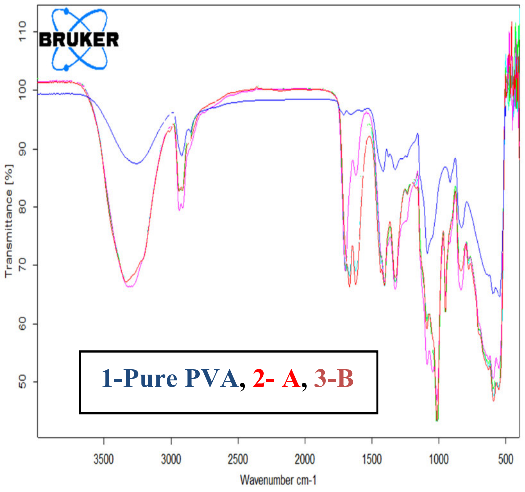

Figure (4): FTIR spectra for pure PVA, A and B

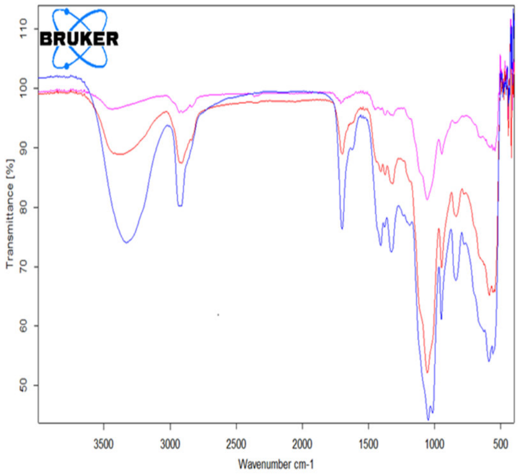

Figure (5): FTIR spectra for A2, A3 and A4

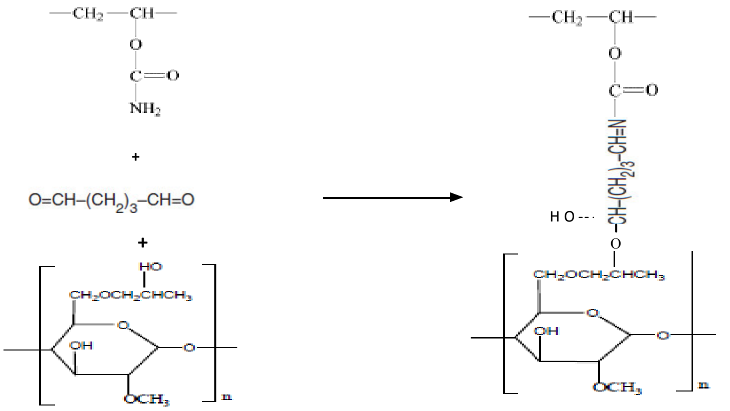

Figure (6): Illustrates preparation polymer hydrogels derivatives

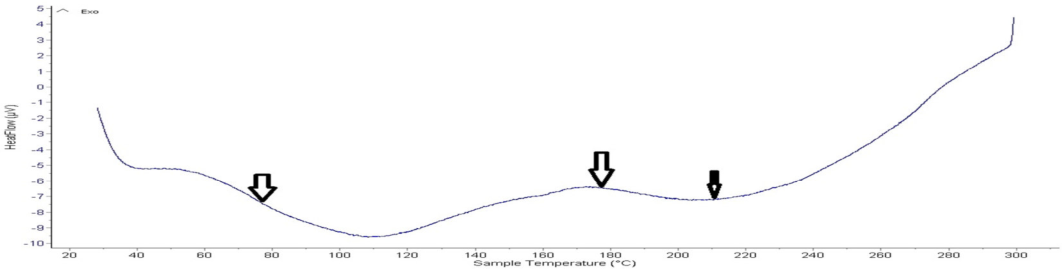

Figure (7): Curves of DSC of pure PVA

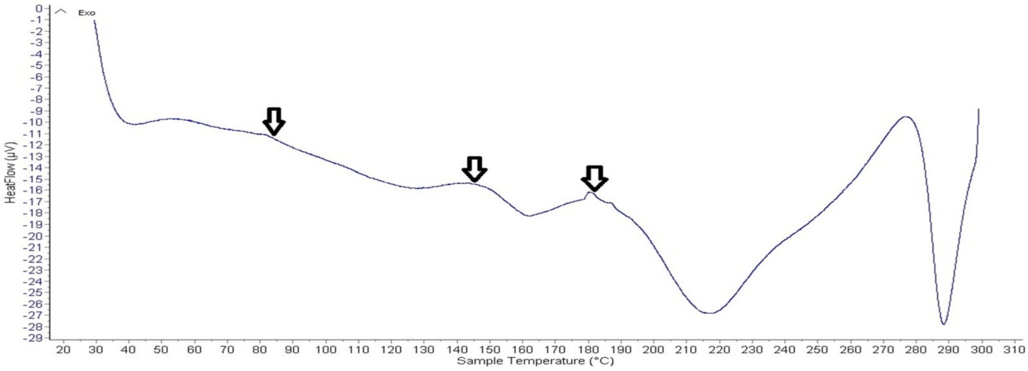

Figure (8): Curves of DSC of sample B

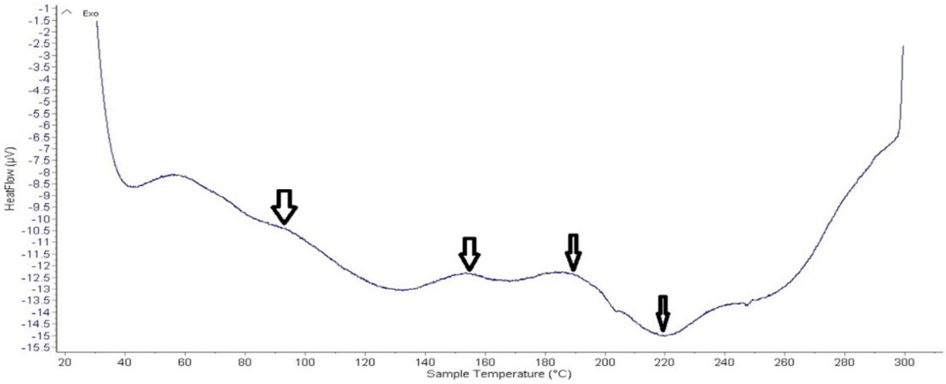

Figure (9): Curves of DSC of sample A

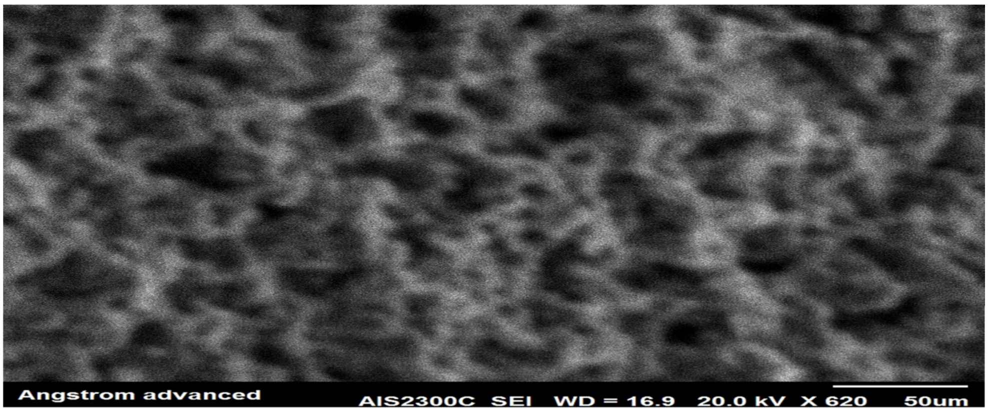

Figure (10): SEM images of sample B1

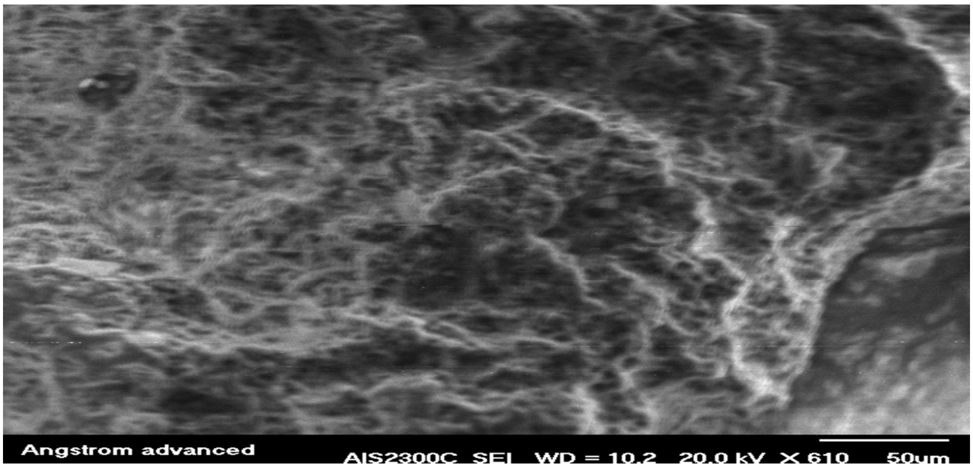

Figure (11): SEM images of sample B3

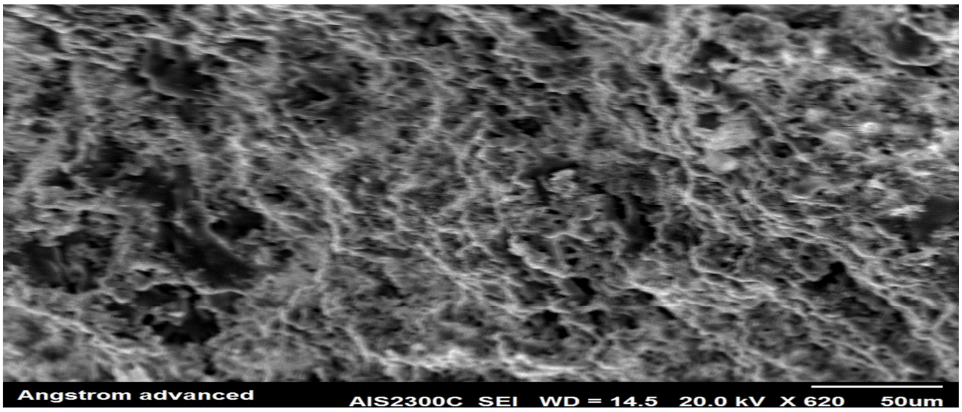

Figure (12): SEM images of sample B4

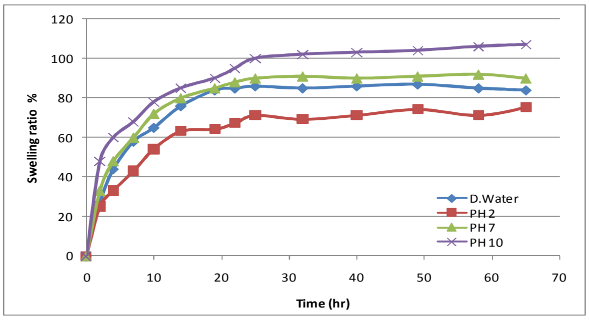

Figure (13): Swelling behaviors of A1 in various pH.

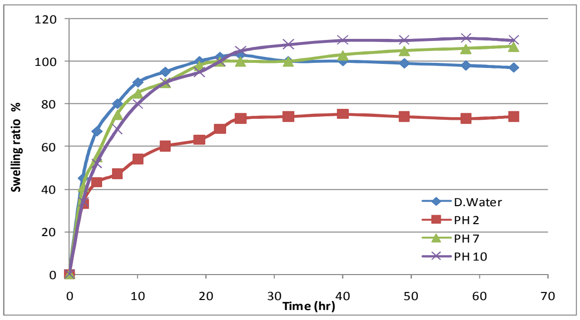

Figure (14): Swelling behaviors of A2 in various pH.

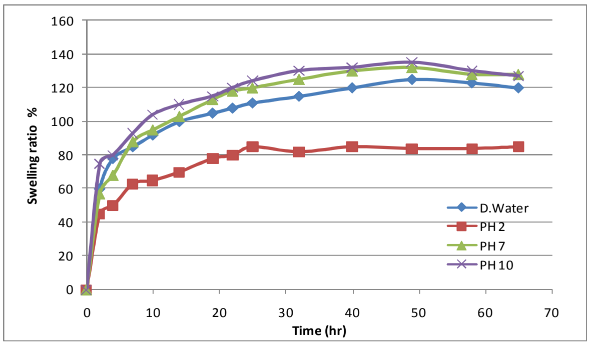

Figure (15): Swelling behaviors of A3 in various pH

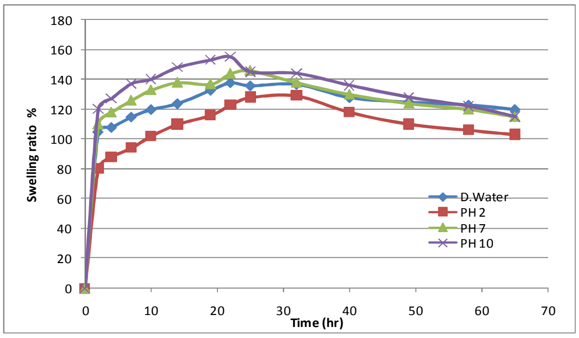

Figure (16): Swelling behaviors of A4 in various pH.

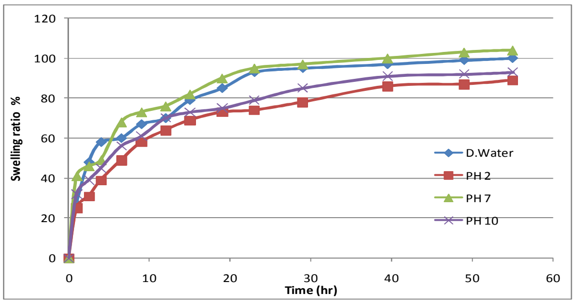

Figure (17): Swelling behaviors of B1 in various pH.

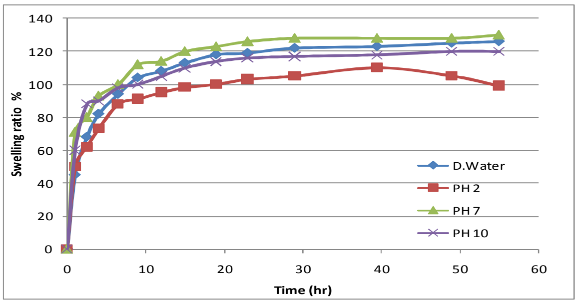

Figure (18): Swelling behaviors of B2 in various pH.

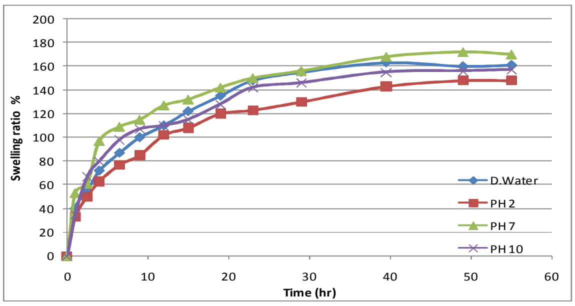

Figure (19): Swelling behaviors of B3 in various pH

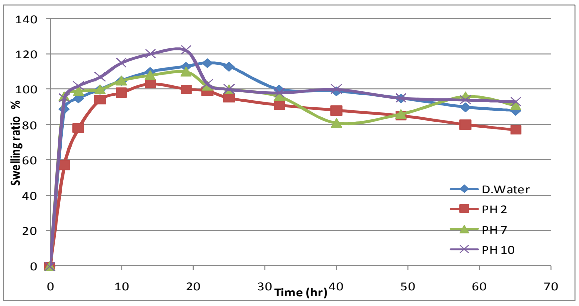

Figure (20): Swelling behaviors of B4 in various pH.