Chemical and Process Engineering Research
ISSN 2224-7467 (Paper) ISSN 2225-0913 (Online)
Vol.52, 2017

Effect of Crosslinking Agent Ratio and Temperature on Degree of Swelling in Polymer Hydrogels

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Abstract
In the present work graft polymers PVA-U were prepared from reaction polyvinyl alcohol PVA and 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 in different ratio 0.5, 0.75, 1.0 and 1.25 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 was observed that swelling ratio of hydrogel decreased by increasing the concentration of glutaraldehyde. The swelling ratio was measured for some hydrogel in pH7 at three different temperatures (25, 37, 50) as function of time, it was observed that swelling ratio increased with increased temperatures..
Keywords: Blend polymers, Hydrogel polymers, PVA, HPMC, Glutaraldehyde

1. Introduction

In recent years, extensive efforts have been devoted to the use of potential pharmaceutical devices such as drug delivery systems which proposes a suitable means of site-specific and/or time controlled delivery of therapeutic agents, among various kinds of drug delivery systems, hydrogel based drug delivery devices have become a major field of research interest. Polymers hydrogel being developed and have shown the most promise. Hydrogels are polymer have three-dimensional crosslinked networks that can absorb large quantities of water without dissolving (Priya& Kapoor, 2013),(Plunkett,2005), (Ray et al. 2010).

Hydrogels resemble living tissues closely in their physical properties because of their relatively high water content and soft and rubbery consistency. Further, the ability of molecules of different sizes to diffuse into (drug loading) and out of (drug release) hydrogels allows the possible use of dry or swollen polymeric networks as drug delivery systems for oral, nasal, buccal, rectal, vaginal, ocular and parenteral routes of administration.(Changez et al.2003),(Mahammad et al.2012). Mostly hydrogels 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.(Ratha et al.2012),(Gajra et al.2012). 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. hydroxypropylmethylcellulose (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 and 50 ml DMSO , 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.

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 in 100 ml deionized water at room temperature with continuous mechanical stirring until clear solution.

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 (1). 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 (1).

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). The swelling behavior of specimen polymer hydrogel A10 was measured swelling in PH7 at different temperatures 25 ^{o}C, 37 ^{o}C and 50 ^{o}C.

3. Results and discussion

Polyvinyl alcohol-Urea were prepared from reaction polyvinyl alcohol with urea, the reaction can are shown in figure (2). Figure (3) 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). FTIR spectrum in figure (4) is associated with sample (A1) crosslinked by glutaraldehyde (PVA-U (A) /GA 0.5). It is observed when cross-linking occurs that the -OH stretching vibration peak and N-H stretch amines (3330-3350 cm^{-1}) was decreased when compared to pure sample (A) and the peak shift towards low wave number from 3338.13 cm^{-1} in sample (A) to 3318.76 cm^{-1} in (A1), This is because of the diminution in the number of-N-H groups and OH groups. In addition, the N-H bend at approximately 1699 cm-1 in the (A2) was increased when compared to pure (A1) (1667cm^{-1}). Figurs. (5) and (6) shows the FTIR spectra of samples A2 and A3 for crosslinked by glutaraldehyde (PVA-U (A) /GA 0.75) and(PVA-U (A) /GA 1.0) respectively, It can be observed that shift peaks towards low wave number to 3318.76 cm^{-1} in A1, 3318.76 cm^{-1} in A2 , 3318.71 cm-1 and 3318.59 cm-1 in A3 for the -OH stretching vibration peak and N-H stretch amines , In addition, the intensity of the absorption band lightly lower (Reis, et al.2006)

Polymer hydrogels derivatives were prepared by reaction PVA-U or blend PVA-U and HPMC with different ratio from glutaraldehyde as crosslinked agent (PVA-U /GA) , figure (7) 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 (8), 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 (9) DSC curve of polymer (A) is shown Tg (92 ^{O}C),Tc (155 ^{O}C), Tm (190 ^{O}C) and Td (220 ^{O}C), The DSC thermogram of compound (A3) is shown Tg (131 ^{O}C),Tc (206 ^{O}C), Tm (235 ^{O}C) and Td (285 ^{O}C) in the figure (10) and when compared this result for polymer (A3) with result of (A) we found shifted and increasing in all value temperature because of interaction between functional groups by used glutaraldehyde as a crosslinking agent and the energy of the endotherms and exotherms increased with increasing crosslinking agent content. Increased glass transition temperature that might improve the drug stability in gastro retentive drug delivery and effectively reduce the premature drug diffusion from the matrix (Trivedi, et al.2015) Figures (11), (12) , (13)and (14) shows the thermal behavior of HPMC, PVA-U and their (PVA-U 50% - HPMC 50%) blends with used glutaraldehyde as a crosslinking agent in different ratios. The compound (A9) there are two peaks Tg 79.2 ^{O}C, Tm 305.4 ^{O}C and the compound (A10) Tg 75.4 ^{O}C, Tm 309 ^{O}C, the compound (A11) Tg 82.9 ^{O}C, Tm 318.3 ^{O}C and the compound (A12) Tg 78.2 ^{O}C, Tm 330 ^{O}C .Where are increase in the melting temperature with increase ratio of glutaraldehyde as a crosslinking agent this well lead to increasing in the density of crosslinking and interaction between functional groups in the polymers and this lead to need to more heating for decomposition of compound when heating. It is well known that the glass transition of the crosslinked polymers depends not only on the main chain rigidity, but also on crosslinking density (Guirguis & Manal 2012).

The changes in surface morphology for the prepared polymer hydrogels was studied by using SEM micrographs. Figure (15) illustrates the surface morphology of sample A1, It can be seen the pure PVA-U with low ratio concetration from Glutaraldehyde as crossliked agent , SEM photos show an increase in the pore average size comparing to those of pore in the A2 hydrogels as shows in Figure (16) due to in sample A2 the ratio concetration of Glutaraldehyde was increase. however, by increasing Glutaraldehyde concentration, new chains will be interaction and changing the morphology of the surface morphology of hydrogels. These changes in surface morphology of polymer hydrogels are due to the creation of new bonds when Glutaraldehyde is added to the polymer as discussed in the FTIR analysis section. As a result of this increase in the ratio concentration of crosslinked agent the pore average size will more decrease in the sample A3 as shows in Figure (17). Also, hydrogels prepared with sample A4 are smooth in morphology shown as figure (18) increase in extent of crosslinker causes the decrease of pore size and decrease in distribution of them. Also the contact surface of hydrogel decreased and swelling decrease, with increasing the extent of cross linker (Patel & Pradeep, 2010).

In hydrogels, the effect of crosslinking depends upon the amount of crosslinking agent used. In this study, different amounts of glutaradehyde were added as crosslinking agent to the hydrogel blend polymers. Figures from (19) to (24) for all sample polymer hydrogels (A1 to A8) show the swelling ratio in different media pH (2, 7, and 10). It was observed that there was difference between the swelling percentages of hydrogel in sample hydrogel polymers due to different concentration of crosslinked agent.

The swelling ratio decreases when increases cross-linked with glutaraldehyde in all mediums, which has been also reported in some other researches (Hezaveh & Ida 2012),(Khalid,et al.2009),(Martínez-Ruvalcaba,

Agustín, et al). These figures are also presented that extent of crosslinking is dependent upon the pH of the media as well as swelling ratio. For instance, in figure (19) the swelling ratio in pH2 for samples A1,A2,A3 and A4 decreased from 76,74,66 and 61 with increasing amount of GA from 0.5, 0.75. 1.0 and 1.25 ml. In figure (20) the swelling ratio in pH7 for samples A1,A2,A3 and A4 decreased from 102, 91, 74, and 70 with increasing amount of GA from 0.5, 0.75. 1.0 and 1.25 ml. In figure (21) the swelling ratio in pH10 for samples A1,A2,A3 and A4 decreased from 114, 107, 100 and 87, with increasing amount of GA from 0.5, 0.75. 1.0 and 1.25 ml.

In general, it is shown that the amount of crosslinking agent of the blend polymer hydrogels affects degree of swelling ratio this is due to increased crosslink density and increased hydrogen bond this lead to decreased pore volume of the network of polymer hydrogels with increasing amount of GA in the matrix. Decrease matrix swelling due to low diffusion of media and decreased water uptake (Rao, et al.2006)

A swelling ratio is affected by change temperature. The study of swelling ratio show in figures from (25) in pH7 for A10 in temperature 25^0C, 37^0C and 50^0C. It was observed that there was difference between the swelling percentages of hydrogel with change temperature. In general, swelling ratio increased with increased temperature.

In figure (25), the swelling results for A10 in PH7 have increased from 105, 128, and 145, respectively with increased temperature from 25^0C, 37^0C and 50^0C, respectively. Certainly, induced crosslinking in this hydrogel have reduced chain flexibility, and reduced water absorption, but when increased the temperature the polymer chains were flexible and increase in temperature caused breaking of secondary interactions, creating more space for water diffusion in the gel matrix and increase water uptake. The solvent tries to penetrate the polymer hydrogels networks to produce three dimention molecular networks at the same time expanding the molecule chain between the crosslinked points, this lead to decreasing the configuration enthalpy value. The molecule in hydrogels network has an elastic contractive force that tries to make the crosslinked contract. When these opposing forces reach equilibrium and the expansion and contraction also reach a balance. The osmotic pressure is the driving force for the expansion of swelling hydrogels, and the network elastic force is the driving force of the contraction of the gel (Mirzaei, et al.2013),(Ahmed & Saeed 2013)

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4. Conclusion

PVA-U were prepared from reaction polyvinyl alcohol PVA and urea. Were blending 8% PVA-U and 5% HPMC in different ratio 100:0, 75:25 and 50:50 with using glutaraldehyde as crosslinked agent in different ratio 0.5, 0.75, 1.0 and 1.25 ml/dl. Studies are made on swelling behavior for all prepared samples in different media of PH (neutral, acidic and alkaline) and deionised water.. It was observed that swelling ratio of hydrogel decreased by increasing the concentration of glutaraldehyde. The swelling ratio was measured for some hydrogel in pH7 at three different temperatures (25, 37, 50) as function of time, it was observed that swelling ratio increased with increased temperatures.

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Table (1): Synthesis derivatives A1 to A12 hydrogels

NO.	PVA-U (A) 8% (ml)	HPMC 5% (ml)	GA25%(ml)	Sulfuric acid 10% (ml)
A1	100	-	0.5	1.0
A2	100	-	0.75	1.0
A3	100	-	1.0	1.0
A4	100	-	1.25	1.0
A5	75	25	0.5	1.0
A6	75	25	0.75	1.0
A7	75	25	1.0	1.0
A8	75	25	1.25	1.0
A9	50	50	0.5	1.0
A10	50	50	0.75	1.0
A11	50	50	1.0	1.0
A12	50	50	1.25	1.0

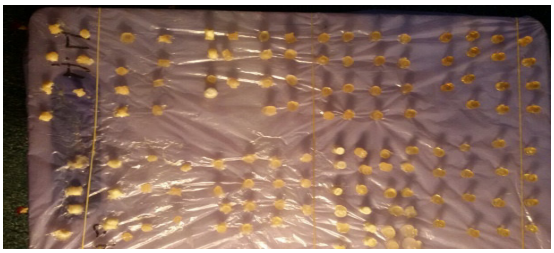

Figure 1. Some prepared specimens polymer hydrogels

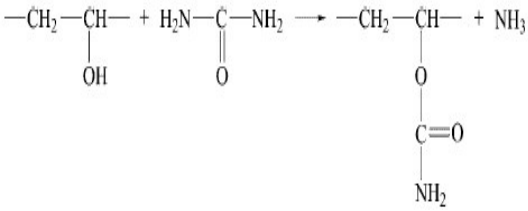

Figure.2.synthesis Polyvinyl alcohol-Urea

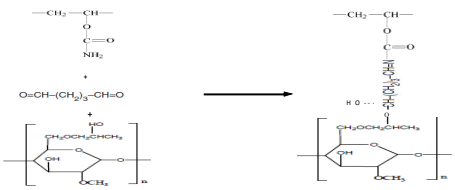

Figure.7. preparation polymer hydrogels derivatives

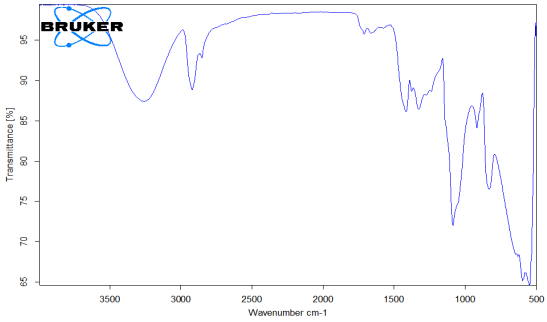

Figure.3. FTIR spectra for pure PVA

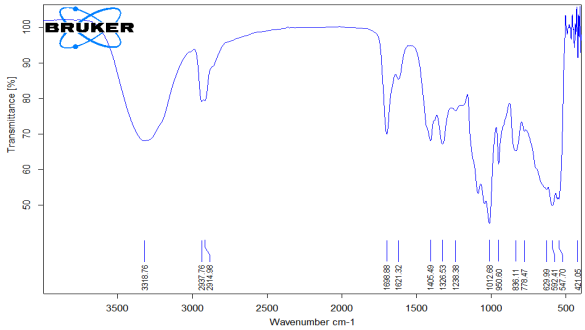

Figure.4. FTIR spectra for sample A1

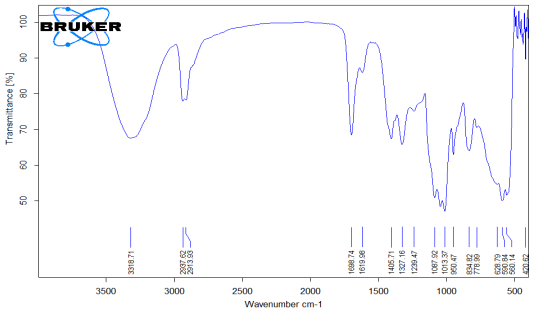

Figure .5. FTIR spectra for sample A2

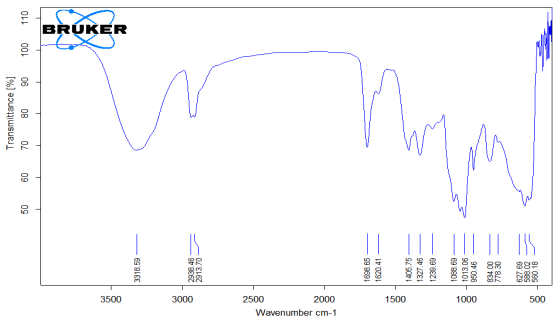

Figure .6.FTIR spectra for sample A3

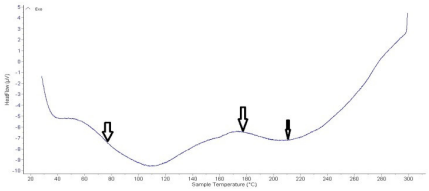

Figure.8. Curves of DSC of pure PVA

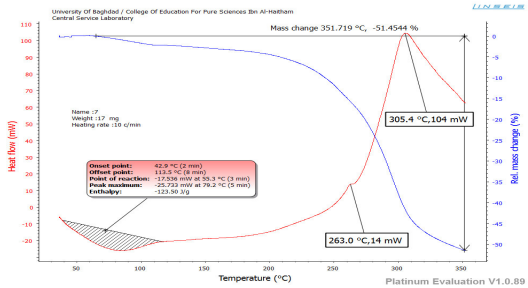

Figure.9.Curves of DSC of sample A

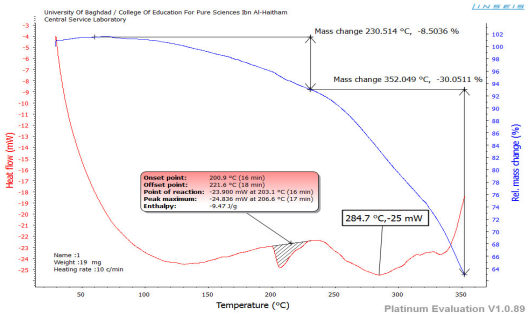

Figure 10 .Curves of DSC of sample A3

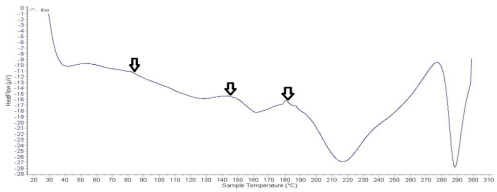

Figure 11. Curves of DSC of sample A9

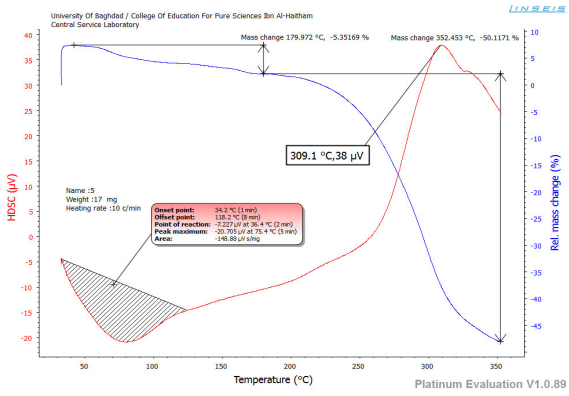

Figure 12. Curves of DSC of sample A10

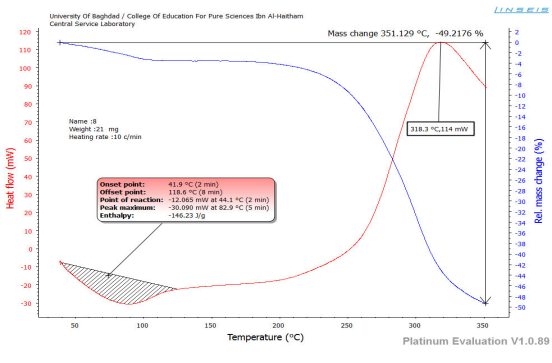

Figure 13. Curves of DSC of sample A11

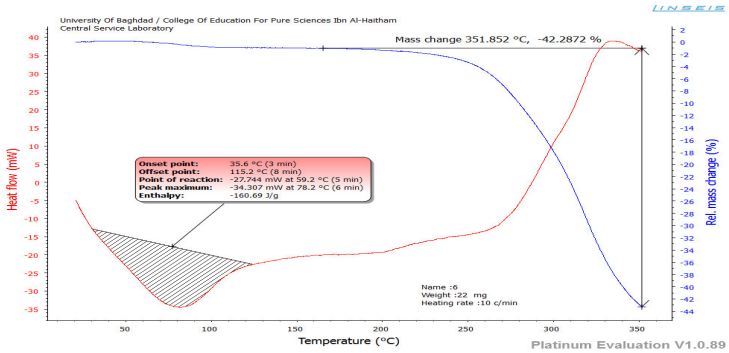

Figure 14. Curves of DSC of sample A12

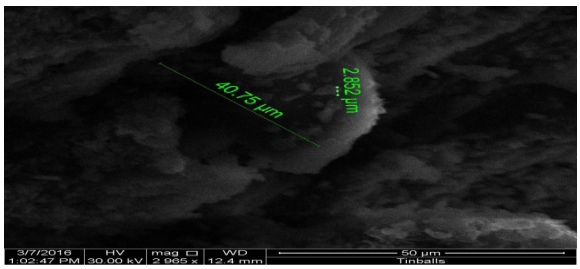

Figure 15. SEM images of sample A1

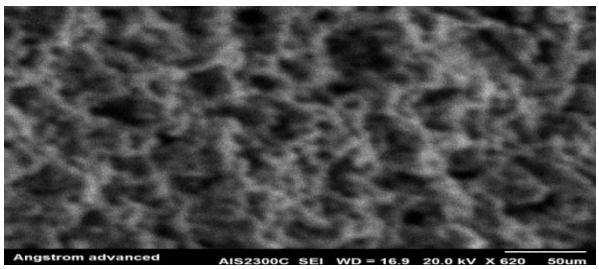

Figure 16. SEM images of sample A2

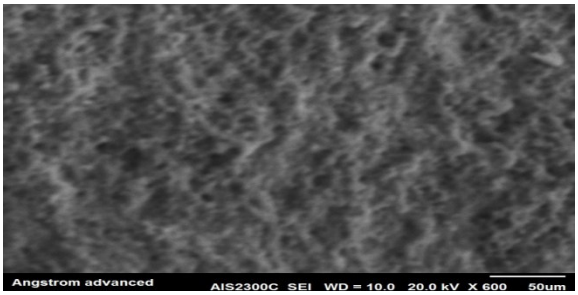

Figure 17. SEM images of sample A3

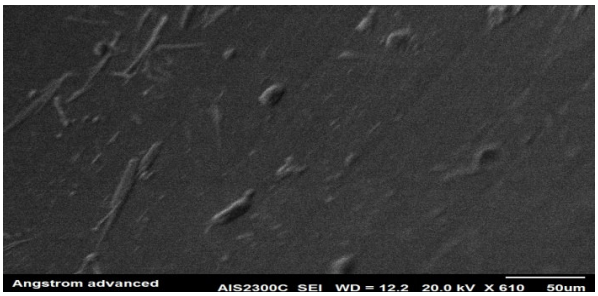

Figure 18. SEM images of sample A4

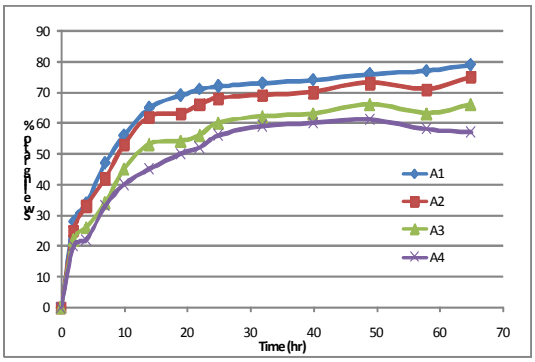

Figure 19. Swelling ratio of (A1 to A4) with different crosslinked ratio in pH 2.

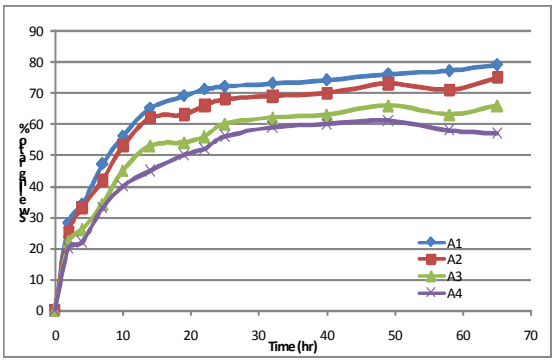

Figure .20. Swelling ratio of (A1 to A4) with different crosslinked ratio in pH7.

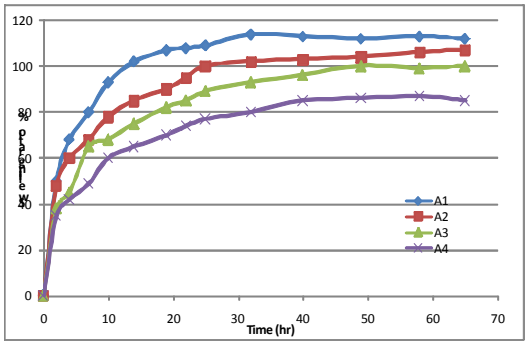

Figure 21. Swelling ratio of (A1 to A4) with different crosslinked ratio in pH 10.

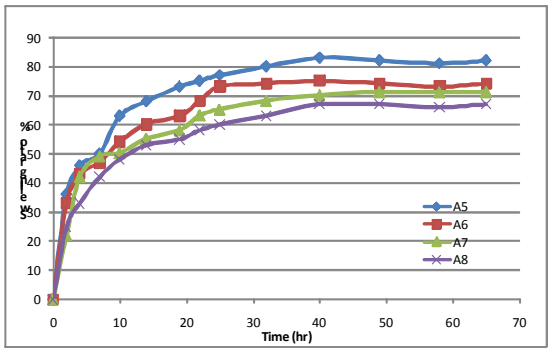

Figure 22. Swelling ratio of (A5 to A8) with different crosslinked ratio in pH2.

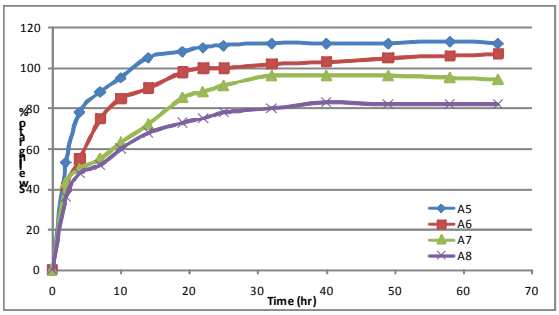

Figure 23. Swelling ratio of (A5 to A8) with different crosslinked ratio in pH 7

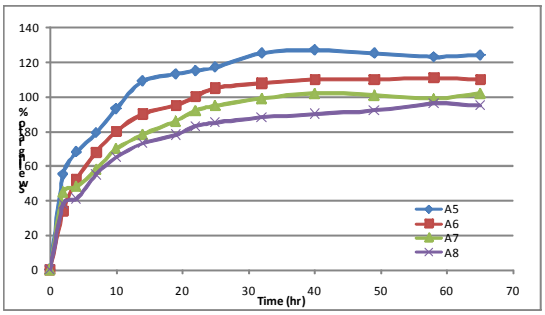

Figure 24. Swelling ratio of (A5 to A8) with different crosslinked ratio in pH10.

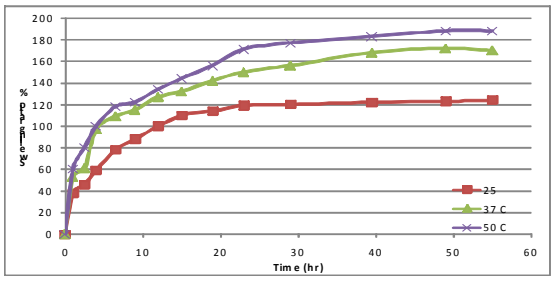

Figure 25. Swelling ratio of (B10) in different temperature at PH7