

Preparation of some new acrylamide copolymers and IPN hydrogels for water storage

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Abstract

Several new copolymers and IPN hydrogel polymers were prepared from acrylamide , diacetone acrylamide , poly (ethylene imine) and glycidyl acrylate by redox polymerization . Ammonium per sulfate was used as initiator and tetramethyl ethylene diamine was used as accelerator .The swelling behavior was studied by determining the swelling ratio (Q) as a function of time . The effect of humidity on the swelling behavior was studied and finally the deswelling characteristic of hydrogels was determined at 45 C⁰ .

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(Q)

Na Cl

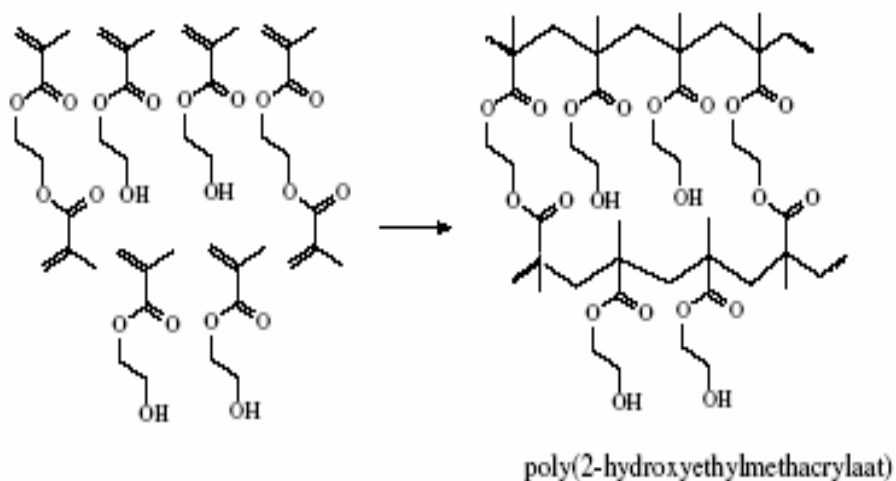
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Introduction

Hydrogels are a three dimensional network of hydrophilic polymers held together by covalent bonds and weaker cohesive forces such as hydrogen or ionic bonds . These networks are able to retain a large quantity of water within their structure , without dissolving . They are glassy in dry state and

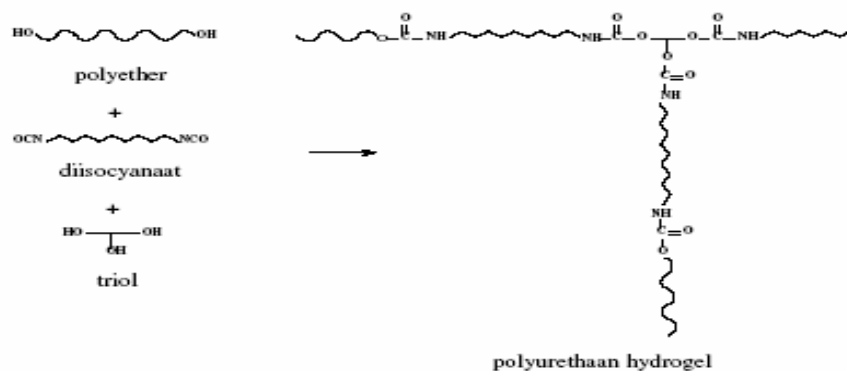
swell in the presence of water to form an elastic gel while preserving their overall shape (Hennink W. et al 2002 ,Que Y. et al 2003 and Kim S. 2002) . In general , the amount of water is at least 20 % of the total weight . If water is composed of more than 95 % of the total weight , the hydrogel is called " superabsorbent " (Chen J. et al 1999) .Hydrogel can be prepared starting from monomers or prepolymers or existing hydrophilic polymers (Schcht 2004) .

Copolymerization of hydrophilic monomers and polyfunctional comonomers , acting as crosslinkers , leads to the formation of hydrophilic network structures . Most commonly used monomers are hydrophilic (meth) acrylate and (meth) acryl amide (Moynihan 1987) . Polymerization of vinyl monomers is most frequently initiated via radical initiators (peroxide , azo – compounds) . Radicals are generated by heating , by the use of redox initiation (e.g. ammonium per sulfat with tetramethyl ethylene diamine) or a photo initiator (Schcht 2004) . The preparation of the hydrogel starting from monomers can be illustrated by following chemical scheme :

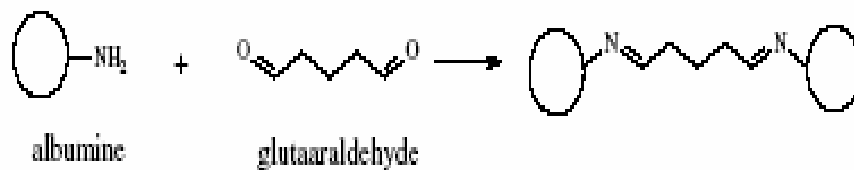


Hydrogel have been prepared by crosslinkage of low molecular weight hydrophilic polymers or oligomers . For example the reaction of poly (ethylene glycol) with diisocyanate in the presence of a triol as

crosslinker (Vanbos M. and Schcht E.1987) . This reaction lead to the formation of crosslinked hydrophilic polyurethane . The hydrogel formation can be represented by the following scheme :



Chemical crosslinkage of hydrophilic polymers leads to formation of hydrogels . For example ,the Sephadex is a network of Dextran crosslinked with epichlorohydrin and proteins are crosslinked with formaldehyde, glutaraldehyde or a polyaldehyde (Eschcht E. et al 1993) . The preparation method of hydrogel starting from hydrophilic polymers can be represented by the following scheme:



Materials and Experiments

Materials

Acryl amide was supplied by (Aldrich Co.) . Bisacryl amide , glycedyl acrylate , diacetone acrylamide and tetramethylethylenediamine were supplied by Fluka Co.) . Poly (Ethylene imine) was supplied by (B.D.H.Co.) .

*Preparation of the copolymers and IPN hydrogels***Preparation of copolymer gels (AD1 – AD3)**

Acryl amide (AcAm) , Diacetone acryl amide (DAAcAm) and bis acrylamide BAcAm) as crosslinker were dissolved in water then (1%) ammonium per sulfate (APS) was added as initiator and mixed well followed by addition of (0.5 %) tetramethylethylenediamine as accelerator at the initiation step with stirring for ten minutes to complete the polymerization reaction . Table (1) shows the quantities of reactants used in the preparation of copolymer hydrogels (AD1 – AD3).

Table (1) : The composition used in the preparation of copolymer gels (AD1 – AD3)

Sample No.	AcAm (g)	DAAcAm (g)	BAcAm (g)	H ₂ O (ml)
AD1	10	10	1	20
AD2	20	10	1.5	30
AD3	30	10	2	40

preparation of IPN gels (AP1 – AP3)

The IPN gels were prepared from acryl amide (AcAm) and poly (ethylene imine) . Table (2) shows the quantities of the IPN gels . The acryl amide (AcAm) , poly (ethylene imine) (PEI) and the crosslinkers (gluteraldehyde and bis acryl amide) were dissolved in water then (1 %) from APS was added followed by addition of tetramethyl ethylene diamine with efficient stirring for ten minutes to complete the polymerization reaction .

Table (2) : The composition used in the preparation of the IPN gels (AP1 – AP3)

Sample No	AcAm (g)	PEI (g)	Gluteraldehyde (g)	BAcAm (g)	H ₂ O (g)
AP1	10	10	0.5	0.5	20
AP2	20	10	0.5	1	30
AP3	10	20	1	0.5	30

Preparation of copolymer gels (AG1 – AG3)

The copolymer gels were prepared from acryl amide and glycedyl acrylate (GA) in different composition from the two components adopting the experimental rocedure described in section (2.2.1) . The quantities of the reactants used are listed in Table (3) .

Table (3) : The composition used in the preparation of the copolymer gels (AG1 – AG3)

Sample No.	AcAm (g)	Glycedyl acrylate (g)	BAcAm (g)	H ₂ O (ml)
AG1	10	10	1	20
AG2	20	10	1.5	30
AG3	10	20	1.5	30

preparation of IPN gels (APG1 – APG4)

The copolymer gels were prepared from acryl amide , poly(ethylene imine) and glycedyl acrylate (GA) in different composition from acryl amide adopting the experimental procedure described in section (2.2.1) . The quantities of the reactants used are listed in Table (4) .

Table (4) : The composition used in the preparation of the copolymer gels (APG1 – APG4)

Sample No	AcAm (g)	PEI (g)	Glycedyl crylate (g)	BAcAm (g)	H ₂ O (g)
APG1	10	2	10	0.5	20
APG2	20	2	10	1.0	30
APG3	30	2	10	1.5	40
APG4	40	2	10	2.0	50

Swelling Studies

Swelling Studies as a Function of Time

The dry samples were allowed to hydrate in the presence of excess amount of distilled water at $(30\pm 5)^{\circ}\text{C}$. The weight of the hydrated samples was measured at different time intervals by removing the gels from water and blotting them to remove the superficial water and weighing them in a closed weighing bottle. Some hydrogels swelled to the extent that they became too fragile to handle. These were placed in a weighing sieve boat. The weighing sieve boat containing the hydrogels was immersed in distilled water for swelling. The weighing boat was taken out to drain the free water from the sieve. The excess of water underneath the sieve was removed by paper towels. Then the weight of the swollen hydrogels was measured by subtracting the boat weight from the total weight.

The swelling ratio (Q) is defined as:

$$Q = (W_s - W_d) / W_d$$

where: W_s is the weight of the swollen hydrogel and W_d is the weight of the dried hydrogels (Chen H. and Hsieh 2001 and Lin J. et al 2001) . Figures (1) - (4) showed the water uptake of the new hydrogels as a function of time.

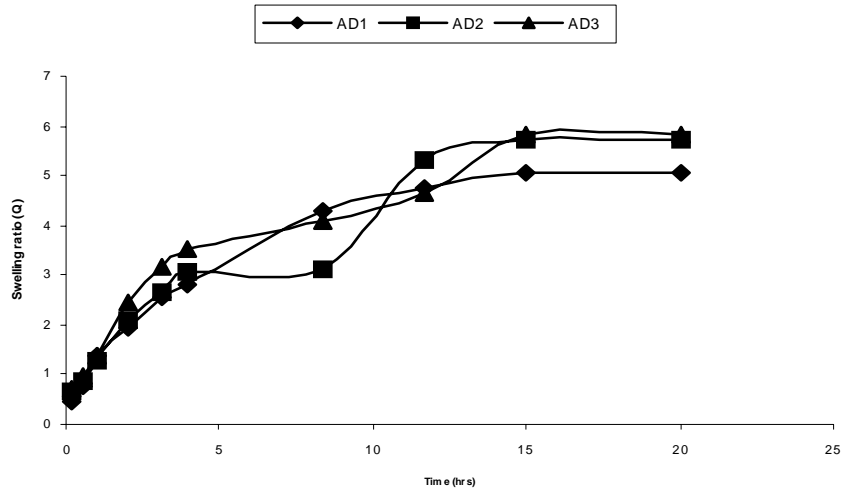


Fig.(1): Swelling ratio for (AD1 – AD3) as a function of time

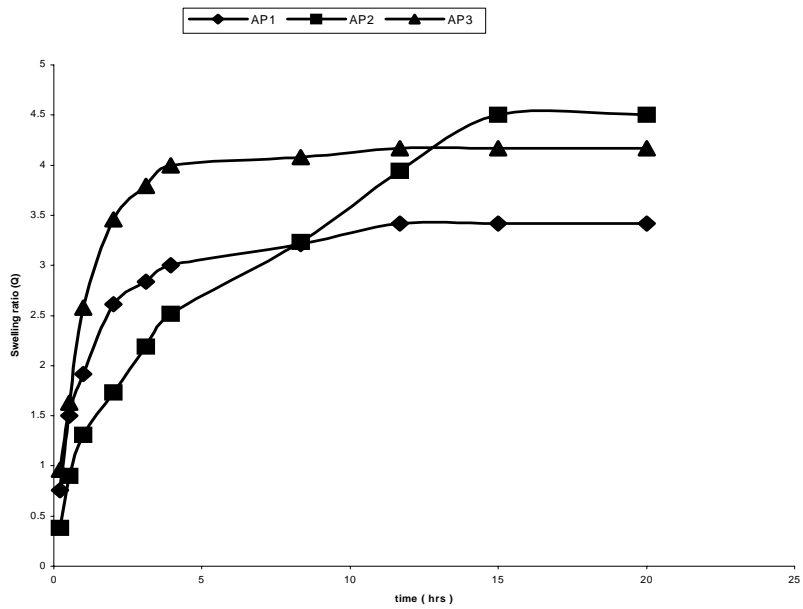


Fig.(2): Swelling ratio for (AP1 – AP3) as a function of time

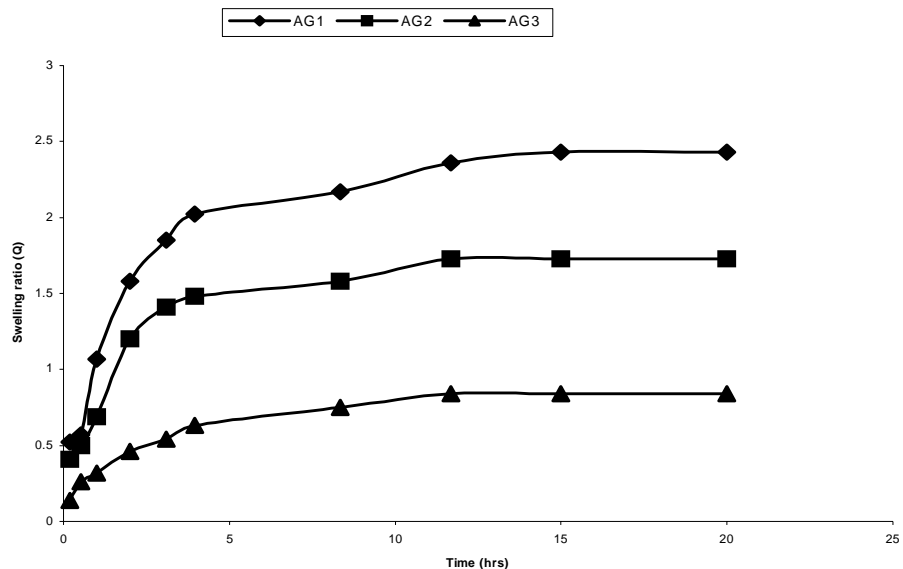


Fig.(3): Swelling ratio for (AG1 – AG3) as a function of time

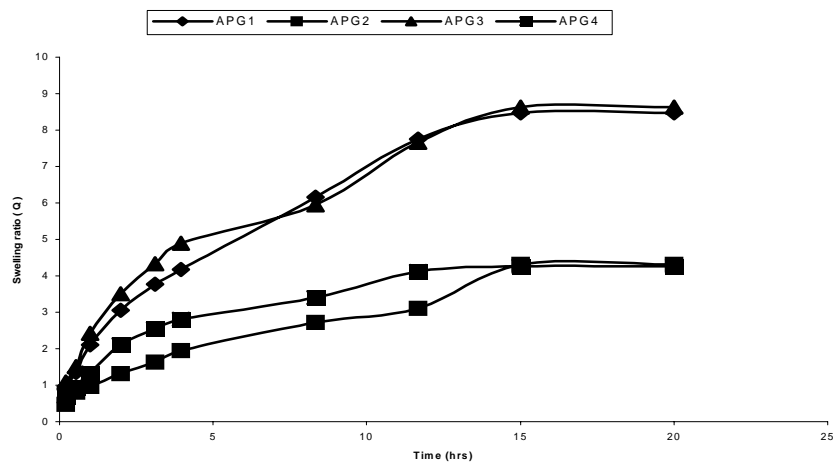


Fig. (4) : Swelling ratio for (APG1 – APG4) as a function of time

The Effect of Humidity on the Swelling Ratio

A simple moistening chamber was built up, as shown in Fig.(5). The dried hydrogels sample was placed in a container supplied with a cap, and sample support, a small amount of water was added to the container. Constant humidity conditions (moisture content) were maintained for the aqueous solutions saturated with appropriate salt. The dried hydrogels were placed on the gel supporters, the hdrogels were removed after 3 days and their weights was measured. The salts used for desired moisture content were: CH_3COOK for 20%, $\text{NaBr}\cdot 2\text{H}_2\text{O}$ for 58%, $\text{NH}_4\text{Cl}+\text{KNO}_3$ for 71.1%, NH_4Cl for 79.3%, $\text{BaCl}_2\cdot 2\text{H}_2\text{O}$ for 88% and $\text{CuSO}_4\cdot 5\text{H}_2\text{O}$ for 98% humidity (Weast R. 1985-1986).

Figures (6) - (9) show (%) water absorbed as a function of humidity percentage.

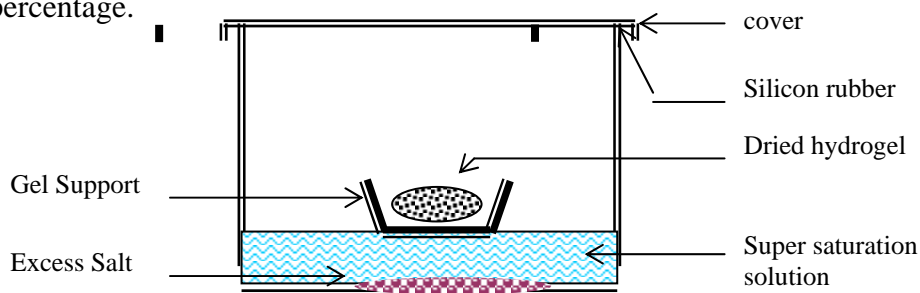


Fig.(5) The designed set-up used to measure the water absorbed at different humidity.

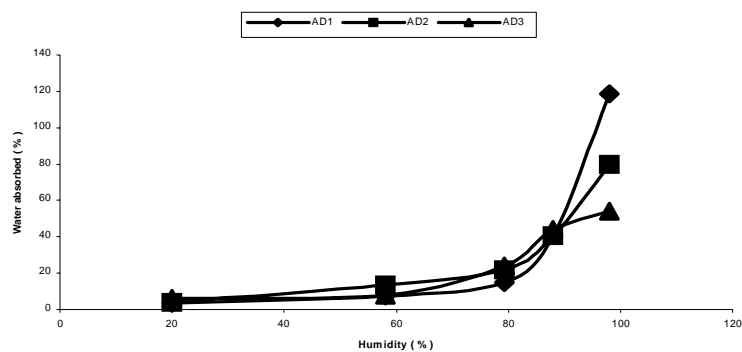


Fig.(6): The effect of surrounding humidity (%) on the water absorbed (%) for (AD1 – AD3)

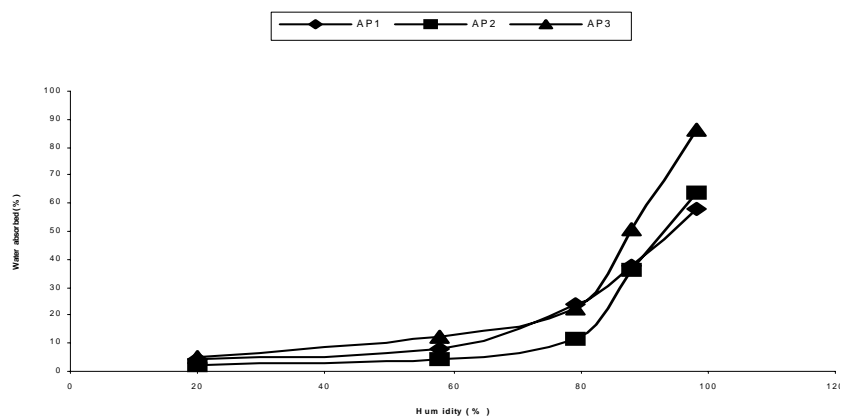


Fig.(7): The effect of surrounding humidity (%) on the water absorbed (%) for (AP1 – AP3)

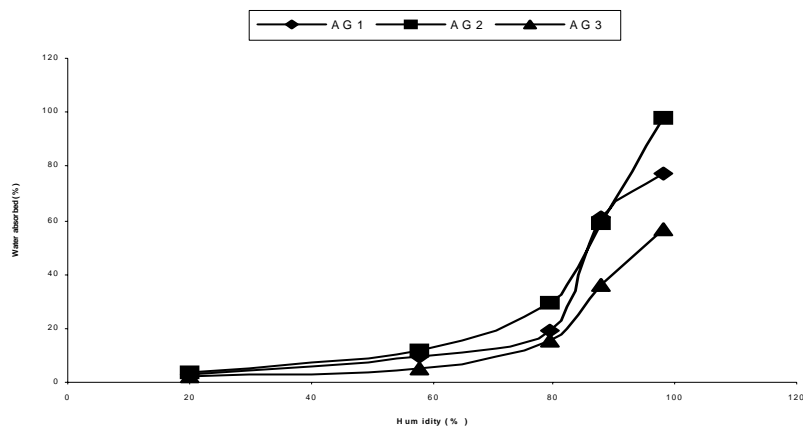


Fig.(8): The effect of surrounding humidity (%) on the water absorbed (%) for (AG1 – AG3)

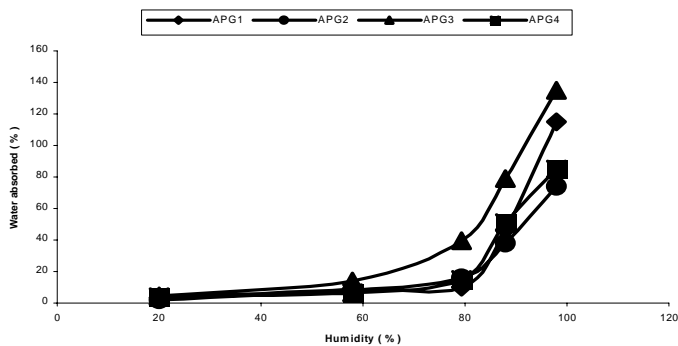


Fig.(9): The effect of surrounding humidity (%) on the water absorbed (%) for (APG1 – APG4)

The effect of NaCl on the swelling ratio

The swelling ratio for the copolymers and IPN gels in the presence several concentration of NaCl salt was examined . Table (5) shows the swelling ratio of the copolymer and IPN gels at several salt concentration .

Table (5) : The swelling ratio of the copolymer and IPN gels in different NaCl ratio

Sample No.	Swelling ratio (Q) in		
	5 % NaCl	10 % NaCl	20 % NaCl
AD1	2.89	3.41	0.82
AD2	3.46	4.10	3.38
AD3	3.60	2.90	3.50
AP1	1.80	2.00	2.40
AP2	3.11	3.25	3.79
AP3	0.86	1.88	2.44
AG1	2.54	3.11	2.60
AG2	2.53	3.00	2.65
AG3	0.31	1.06	0.95
APG1	3.83	3.74	4.93
APG2	4.50	3.00	4.00
APG3	2.21	4.44	4.36
APG4	3.85	5.13	3.44

Deswelling Studies

The swollen hydrogels were dried for 24 hours under blowing warm air (45 ± 1)°C (Chrila et al 1993). Figures (10)-(13) show the deswelling behavior as a function of time.

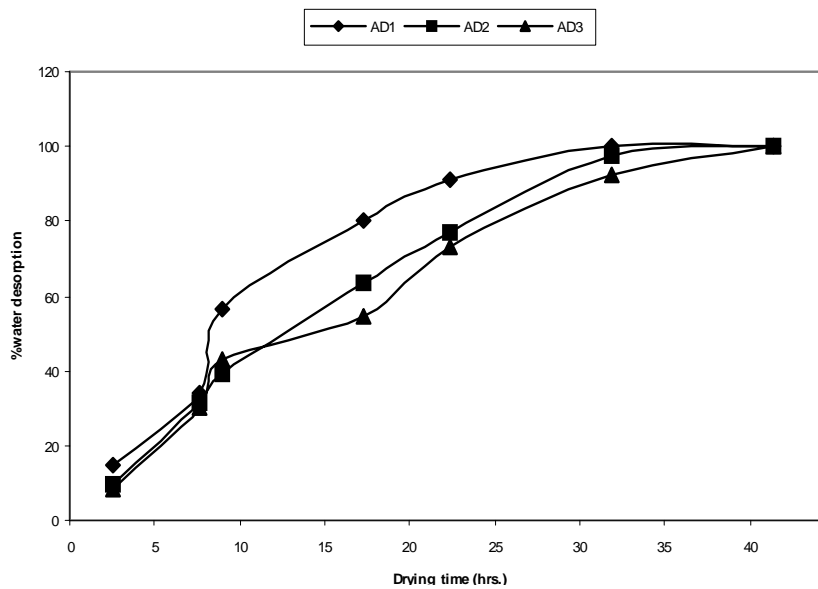


Fig.(10): The effect of drying time (hrs) on the water desorption (%) For (AD1 – AD3)

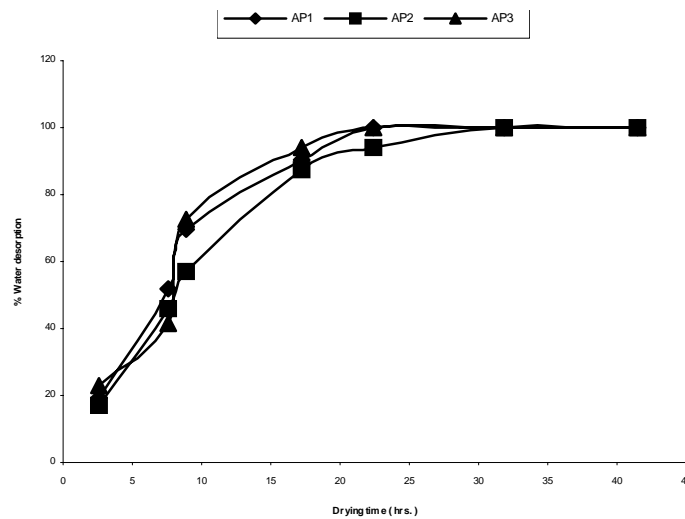


Fig.(11): The effect of drying time (hrs) on the water desorption (%) for (AP1 –AP3)

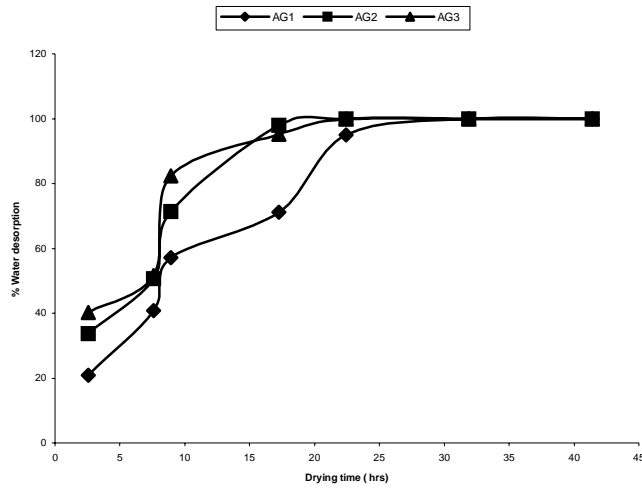


Fig.(12): The effect of drying time (hrs) on the water desorption (%) for (AG1- AG

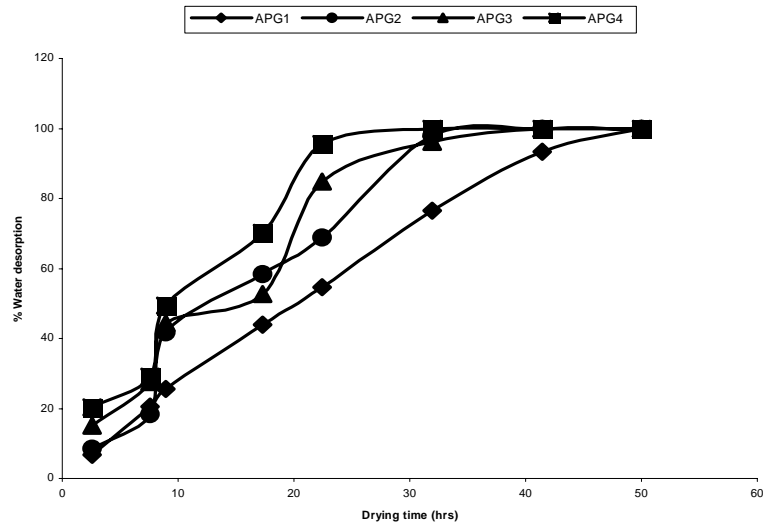
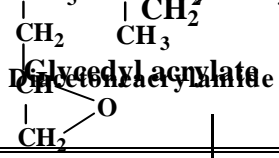


Fig.(13): The effect of drying time (hrs) on the water desorption (%) for (APG1 – APG4)



Glycedyl acrylate APS TMED

~~Result of APS / TMED~~

The monomers used in this study can be gelled quite fast in the aqueous solutions in the presence of (ammonium per sulfate APS / tetra methyl ethylene diamine TMED) as initiator . The gelation can take place even at low temperature . The decomposition of APS / TMED redox initiator in aqueous system is greatly accelerated by the presence of reducing agents. APS/TMED initiators the gelation process within a minute when used at a concentration of about 1% (wt/wt) of the monomer and for several minutes when used at a concentration less than 0.5% (wt/wt) . Formation of the copolymeric hydrogels can be represented by the schemes (1-3) :

Schem (1) : Formation of the copolymeric hydrogels (AD1 - AD3 from acrylamide, Diacetoneacrylamide and bisacrylamide as crosslinking agent .

Schem (2) : Formation of the copolymeric hydrogels (AG1 - AG4) from acrylamide, glycedyl acrylate and bisacrylar crosslinking agent
Schem (3) : Formation of the copolymeric hydrogels (APG1 - APG4) from acrylamide, glycedyl acrylate Poly(ethyleneimine) and bisacrylamide as crosslinking agent .

The IPN gels (APG1 – APG4) consist of two polymer chains , the first chain can be formed from poly (acryl amide) crosslinked by bisacrylamide and the second chain from poly (ethylene imine) which crosslinked by gluteraldehyde to form the instantaneous IPN's . Fig.1 shows , that the swelling ratio independent of the constituents acryl amide in the three different ratios studied . In copolymer gels (AP1 – AP3) ,the swelling ratio increases with increasing the ratio of acryl amide or poly (ethylene imine) but in copolymer gels (AG1 – AG3) , the swelling ratio increases while using the stoichiometric amount from acryl amide and glycedyl acrylate but generally , the swelling ratio increases with increasing the acryl amide constituent , while the high swelling ratios were obtained with IPN gels (APG1 – APG4) .This can be related to increase the number of hydrogen bonding between the copolymer and IPN gels with water . During the experimental work it was noticed that, when the dried hydrogels were placed in water, the outer region swelled to equilibrium very rapidly only few seconds after contact with water. Then due to penetration of water, the clear region gradually expanded towards the center but this penetration step was quite slow. On the other hand the studied hydrogel resins showed an interesting efficiency to absorb water from the surrounding atmosphere. At low moisture content (20-58)%, the percentage of water absorbed by the dried gels was less than (20%) of the total weight while at high moisture content (> 80%), the percentage of water absorbed by the dried gels was dramatically increased and reached to about (40 - 114) % of the total weight .

Table (5) shows the effect of NaCl concentration on the swelling ratio . In general , all of the copolymeric and IPN gels showed higher swelling ratio in distilled water than in the presence of the NaCl salt . On the other hand , substantial changes in the swelling ratios were observed in the 10 % (wt/ v) NaCl concentration . This behavior can lead to use these copolymeric and IPN gels as sensors to the presence of NaCl in the solutions (Haddad A. et al 2002) .

Finally , the data concerned with desorption presented in Fig. (10 – 13) showed that the rate of water desorption for most of the gels was medium ,

indicating the water storage capability for higher than ten hours at 45 C⁰ accordingly these hydrogels could be recommended for agriculture applications .

References

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