



# Hydrophilic Monomers Graft Gum Arabic Hydrogels Prepared in Different Cross-linking Nature and Study of their Effects on Irrigation of Agriculture Soil

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## Abstract

Gum Arabic (GA) was grafted with acrylic acid (AA), acrylic acid and acrylamide (AAM) mixture, or AA and AAM and N-Vinyl pyrrolidone (VP) mixture. The polymerization process was initiated with ammonium persulphate (APS) and cross-linked, either chemically using N,N'-methylenebisacrylamide (MBA) or physically, where sodium hexameta polyphosphate (SHMP) was used. Degree of swelling (DS) of the prepared superabsorbent polymers were measured in deionized water, river water (around 400 ppm hardness) and in artificial hard water prepared with different concentrations of CaCl<sub>2</sub> or MgSO<sub>4</sub> salt solution. Suitable weight percentage of the hydrogel was mixed with Sandy Soil and studied, for increasing the degree of saturation of Sandy Soil with water, and to extend the time of Sandy Soil water-retention percentage (WR%). Different characterizations of both, starting materials and prepared hydrogels were investigated using different Instrumentals. The FTIR spectroscopy identifications of the important functional groups of both raw materials and prepared hydrogels have shown that grafting of the used monomers on the main polymer chains were occurred. Whereas, XRD technology has shown very intense and sharp peaks, which improve the highly crystalline structure of the hydrogel. Scanning electron microscopy SEM measurements of the hydrogels were provided good quantitative analysis about the elemental compositions and their total percentages in hydrogel, in addition to their morphological images. Thermal analysis including differential scanning calorimetry DSC, and thermogravimetric analysis TGA were studied carefully for both raw materials and their formed hydrogels. In generally an increase in thermal stability were found for produced hydrogels.

**Keywords:** Superabsorbent polymers; Hydrogels; Gum arabic; Swelling behavior; Water- retention; sodium hexameta polyphosphate SHMP.

## Introduction

Superabsorbent hydrogel polymers SAPs can use their homopolymers or copolymers to form three-dimensional strong networks able to absorb and keep a significant quantity of aqueous fluids even under some pressure, and preserve its physical structure<sup>1,2</sup>. Superabsorbent materials can carry huge amount of water and swell without dissolving<sup>3</sup>. The polymer chains are maintain connect with each other in hydrophilic polymer by cross-links of covalent bonds beside hydrogen bonding as ionic forces or through hydrophobic interactions<sup>4</sup>.

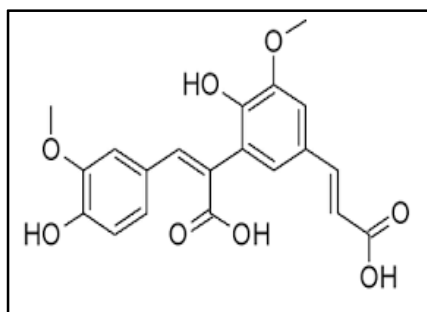
The most SAPs used in the market are produced from Acrylic acid (AA) and its sodium or potassium salts, beside acrylamide (AAM) hydrogel<sup>5</sup>. However, although acrylamide based hydrogels are the most common hydrogel, but they lack hydrolytic stability which can be increased if substituted acrylamides have alkyl or hydroxyl alkyl groups<sup>6</sup>. N-Vinyl pyrrolidone (VP), the water-soluble monomer, its polymer is great flexible and highly compatible, both in solution and film form, with most inorganic salt solutions and with many natural and synthetic resins<sup>7,8</sup>.

Natural gums are used in huge in the synthesis of SAP and was reported in this regard the use of Tara gum in presence of acrylic acid and initiated by gamma radiation<sup>9</sup>. Acacia gum (AG) and poly (methyl methacrylate) (PMMA) have been prepared by graft polymerization use ceric ammonium sulphate as initiator was investigated<sup>10</sup>.

Natural material and their properties such as, compatibility, biodegradability, high hydrophilicity and low production cost, are suitable properties may important to share synthetic material like acrylate monomers in preparation of a superabsorbent polymer<sup>11-13</sup>.

Gum arabic (GA) is a branched, neutral nonionic polysaccharide, its backbone consist of arabinogalactan, the biopolymer which consist of arabinose and galactose monosaccharide, which exist in the furanose configuration. Galactan portion have 30 units with alternating ( $\beta$ -(1-5) and ( $\beta$ -(1-6) glycosidic linkage. Arabinane chain have about 30 residues connected with galactan chain at three branch points, at residues 8, 10 and 12, is a complex branched structure. The arabinane glycosidic linkages have  $\alpha$ -(1-3),  $\alpha$ -(1-5) and ( $\beta$ -(1-2)

and the main glycosidic linkage of the arabinane<sup>14</sup>. Gum Arabic monosaccharide is covertly linked with 8-5`noncyclic diferulic acid as shown in Figure-1.



**Figure-1**  
**Structure of 8-5`noncyclic diferulic acid**

The natural gums have the ability to be good reinforcement as fibers in polymer matrices<sup>15</sup>, hydrophilicity and swelling in cold water, forming viscous colloidal dispersions or sols and easily available and biodegradable<sup>16</sup>.

In present work, superabsorbent polymers are prepared by graft polymerization of gum arabic with sodium salt of acrylic acid only or with mixture consist of acrylic acid and acrylamide, or acrylic acid and acrylamide and N-Vinyl pyrrolidone monomers. Ammonium persulphate was used for initiation of free radical graft polymerization. N,N`-methylenebisacrylamide and sodium hexameta polyphosphate cross-linkers were used for chemical and physical cross-linking of the prepared SAP's, respectively. The prepared hydrogels were mixed in low weight percentages with Sandy Soil in order to increase its water absorbency and in the same time to elevate the water-retention percentage of the soil used in agriculture.

## Methodology

**Raw materials:** Acrylic acid (AA, Chemically pure, CAS, Himedia Laboratories Pvt. Ltd., India) was purified by distillation under reduced pressure. Acrylamide (AAM, Fluka, Switzerland) crystallization in acetone was used for purification. Gum arabic (GA, BDH, U.K) was of food grade. Ammonium persulphate (APS, analytical grade, supplied by PURE, U.S.A). N-vinyl pyrrolidone (VP, BDH, U.K) was purified using distillation under reduced pressure. N,N`-methylenebisacrylamide (MBA, Fluka, Switzerland) was recrystallized from methanol. Sodium hexameta phosphate (SHMP), sodium hydroxide (NaOH), calcium chloride (CaCl<sub>2</sub>) and magnesium sulphate (MgSO<sub>4</sub>) were analytical grade, supplied by (BDH, U.K). Other chemicals are obtained commercially and used without further purification. Preparation of alkaline pyrogallol solution for removal of dissolved oxygen during graft polymerization was prepared according to the standard methods<sup>17</sup>.

**Preparation of superabsorbent polymers:** Different types of

SAPs were prepared. Gum arabic was grafted via free radical polymerization with sodium acrylate alone, or grafted with a mixture of sodium acrylate and acrylamide, or a mixture of sodium acrylate, acrylamide and N-vinyl pyrrolidone. According to maximum degree of swelling, SAPs were prepared after testing many mole fractions or concentrations of GA and its grafted monomers or APS initiator and MBA or SHMP cross-linkers.

4.0mL of (1.25, 2.5, 3.75, 5.0 or 6.25) %w/v of gum arabic (GA) was heated to 65°C in a 250 mL flask connected to a reflux condenser, a thermometer and nitrogen line passed on alkaline pyrogallol solution for free of oxygen. 10mL of various concentrations of APS initiator (3.0, 4.0, 5.0, 6.0 or 7.0) %w/v was added to GA solution. 10min the solution was leaved at 65°C inside the flask. Grafting of GA chains was performed through the addition of the following solutions:

(3.0,5.0, 7.0, 9.0 or 11.0) mL of 85% w/v sodium acrylate, prepared by neutralization of AA in 8.0 mole /L NaOH solution were added for preparation of (GA-g-AA) SAP.

7mL of 85% w/v sodium acrylate in addition to (0.5, 1.0, 1.5, 2.0 or 2.5) mL of 50% w/v AAM in deionized water solution were added for preparation of (GA-g-AA&AAM) SAP.

7 mL of 85% w/v sodium acrylate and 2 mL of 50% w/v AAM solution in addition to (1.0, 2.0, 3.0, 4.0 or 5.0) mL of 50% w/v VP in deionized water solution were added for preparation of (GA-g-AA &AAM&VP) SAP.

8.0 mL of (2.0, 3.0, 4.0, 5.0 or 6.0) % w/v of MBA chemical cross-linker or 7 mL of (14.3, 28.6, 42.9, 57.0, 71.4 or 114.3) %w/v of SHMP physical cross-linker were both prepared in deionized water and added individually to the previous graft solution. Finally, the heat of GA mixture which was in three necked flask was depressed from 65°C to 40°C, then final mixture of graft monomer and cross-linker was added gradually and the reaction temperature was increased another time to 75°C slowly and was kept at that temperature for 3h with continuous stirring. Final polymer product was kept overnight at 40°C in vacuum oven<sup>18</sup>. Dried polymer after vacuum oven was washed directly with deionized water more than one time, for removal of unreacted materials. The polymer was leaved in the washing medium for 48h, filtered and dried at 40-50°C in a vacuum oven overnight and finally grinded and passed through 50 mesh sieve for production of tiny particles.

**Characterization of the superabsorbent polymers: (FTIR) analysis:** The Fourier transform infrared (FTIR) spectra were performed on a Bruker Co. Fourier- Transform Infrared Spectrophotometer, Germany, 2003, in 4000-400cm<sup>-1</sup> region in the form of KBr pellets, to detect the functional groups of the SAP's.

**X-ray diffraction XRD analysis:** XRD analysis of (GA-g-AA)

hydrogel cross-linked physically was recorded up to  $2\theta$  scale in an angle range of  $5^\circ$ - $90^\circ$  at a scan speed of  $1^\circ \text{ min}^{-1}$  using X-ray diffractometer (XRD- Panalytical, Netherlands, 2013) using copper Indium (0.9/0.1) 100% radiation target and nickel filter at a current of around  $20\mu\text{A}$  under a voltage of 35Kv.

**Scanning electron microscopy (SEM) analysis:** SEM images of some hydrogels and their quantitative element analysis were studied. Hydrogel particles were mounted on aluminum studs using double adhesive tapes and coated under vacuum by exposing to beam sputter of a gold ion 40 sec. and at 25mA (PELCO S.C.6 ).The SEM model (TESCAN, Czech Republic, 2011) was used for detection the images.

**Thermal measurements:** Thermogravimetric analysis (TGA) and differential scanning calorimetric (DSC) analysis were detected on a TG analyzer (TG/DTA-SDT Q600 V20.9 build 20) under a nitrogen atmosphere and subjected to heating at a rate of  $10^\circ\text{C}/\text{min}$  in the temperature range of 25- $550^\circ\text{C}$ .

**Estimation of the superabsorbent polymers: Measurement of degree of swelling (DS) of SAP's:** The pre-weighted dry SAP was plunge in swelling medium (deionized water, river water or salt solution) and kept no more for 24h at room temperature for equilibrium swelling. The swollen SAP polymer was filtered in a sieve of 100 meshes and kept for 20 min for removal of free water. The swollen SAP was weighted and the change in their mass will represent the equilibrium water absorption which can be calculated as degree of swelling (DS) using the following equation

$$\text{Degree of Swelling (DS) } g/g = W_1 - W_0 / W_0 \quad (1)$$

Where  $W_1$  is the weight of the sample after swelling and  $W_0$  is the weight of dry sample.

Tagret river water was collected near Mosul city from river bank, and its hardness was 400 mg/L (400 ppm) which was calculated according to the EDTA methods<sup>19</sup>. This type of water was also used as swelling medium for calculation of DS of prepared SAPs. In addition, salt solution which was used for calculation of DS for comparison was prepared from different concentrations of  $\text{CaCl}_2$  (0.9, 1.8, 2.7, 3.6, 4.5, 5.4, 6.3, 7.2, 8.1 and  $9.0 \times 10^{-3}$  M, and of  $\text{MgSO}_4$  (0.82, 1.66, 2.49, 3.32, 4.15, 4.98, 5.81, 6.65, 7.48 and  $8.3 \times 10^{-3}$  M, which represent the salt concentration of  $\text{CaCl}_2$  and  $\text{MgSO}_4$  starting from 100 -1000 ppm which could be cover most of the hardness scale of irrigation water.

**Measurement of DS at different pH:** Solutions with acidic and basic pHs were prepared Individually using different buffer solutions to achieve pH solutions having pH at 5, 6, 7, or 8. Where these pHs are near sandy soil pH that its rang is between 6.5-8. The pH values were checked by a pH meter. Then, 0.1g of dried SAP was added for achieve swelling measurements according to Equation-1.

**Measurement of degree of saturation of sandy soil:** 200g of dry sandy soil was mixed with (0.5, 1.0 or 2.0) g dried polymer and kept in ventilated paper cups. Then, rain water was added until the soil sample reaches its saturation point. The saturation point of the sample was reached by seeing the rainwater seeped out from the bottom of the cup<sup>20,21</sup>. A reference cup was prepared under the same conditions except no polymer was present. The total weigh of saturated soil was recorded. The soil sample was dried at  $102^\circ\text{C}$  and for 24h inside oven. Pre-weight the cold sample after it was dry and the degree of it saturation with water was calculated using the following equation.

$$\text{Degree of saturation (g/g)} = W_2 - W_0 / W_1 \quad (2)$$

Where  $W_2$  represent total weight of sandy soil at saturation point,  $W_1$  is the weight of dry sample in the oven after 24h,  $W_0$  is the original weight of sandy soil mixed with polymer before irrigation with rainwater.

**Measurement of water-retention percentage of mixture of soil and SAP:** In ventilated paper cup a sample of 200g of dry sandy soil was mixed with 1g of dried SAP where the polymer was immersed under 1 cm depth of sandy soil surface. After that 100 mL rainwater was added slowly, which represent 3mm rain fall level in most arid and semi-arid regions<sup>20,21</sup>. The tested cups were maintained at almost  $20^\circ\text{C}$  and in air humidity not more than 25%. One reference cup was prepared under the same conditions except has no polymer. The cups were weighted daily and the water-retention percentages (WR%) were calculated according to the following equation.

$$\text{Water- retention \%} = W_t / W_0 * 100 \quad (3)$$

Where  $W_t$  represent a daily decrease in the total cup weight, and  $W_0$  is the initial weight of cup.

## Results and Discussion

**Synthesis and characterization of SAP's:** Three types of superabsorbent polymers were prepared. Gum arabic (GA $\equiv$ 1) was representing the main polymer chains, and acrylic acid (AA $\equiv$ 2), acrylamide (AAm $\equiv$ 3) and N-vinylpyrrolidone (VP $\equiv$ 4) were used for grafting the main polymer chains of GA. The following superabsorbent polymers were prepared and cross-linked chemically (CH) and physically (PH) and as follows: (GA-g-AA) cross-linked chemically (12CH) and physically (12PH); (GA-g-AA&AAm) cross-linked chemically (123CH) and physically (123PH); and finally (GA-g-AA&AAm&VP) cross-linked chemically (1234CH) and physically (1234PH).

Maximum degree of swelling (DS) was depended in selection the suitable mole fractions of the raw materials used in preparation of different SAPs and suitable concentration of the polymer initiator, type of cross-linkers and their concentrations. DS was also depended in estimation the type of swelling water used (deionized water, river water and salt solution), and to

record notifications about the physical or chemical changes occurred, and their effects on maximum degree of swelling.

Characterizations of the prepared SAP hydrogels were done for their structure, presence of active groups, morphologies, quantitative element analysis, surface porosity, crystallinity and their thermal stability. FTIR, XRD, SEM and DSC-TGA techniques were used for that purpose.

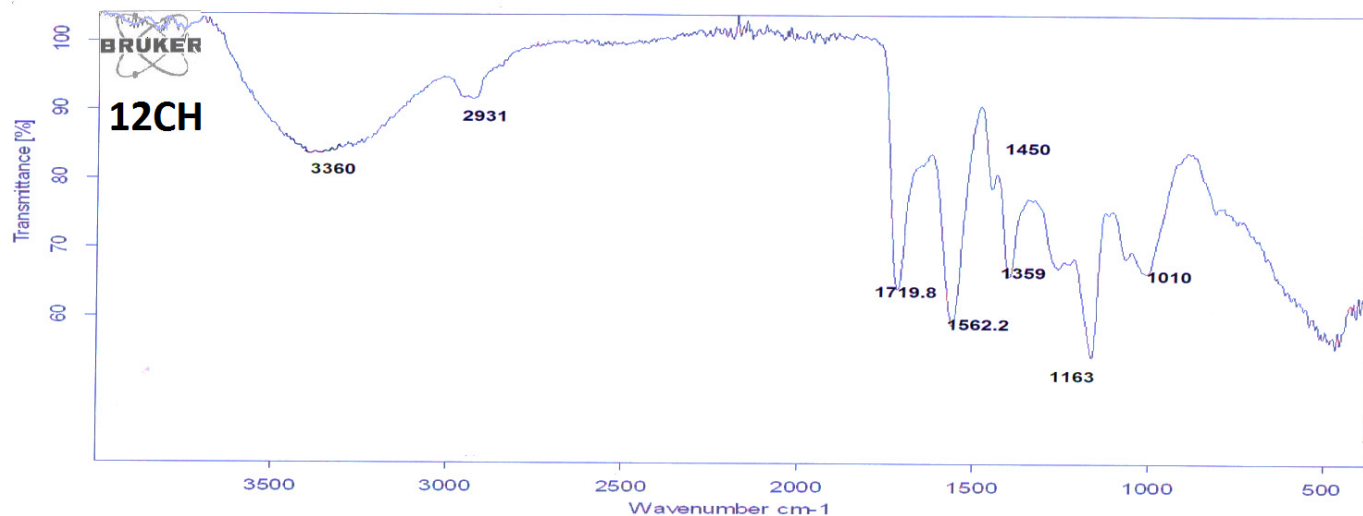
Samples with good physical, chemical and mechanical properties were selected and mixed with suitable percentage of sandy soil and tested in their degree of saturation and water-retention percentage with time.

**FTIR analysis:** FTIR characteristic frequencies at specific bands, Table-1, and some are shown along the IR spectra, Figure-2 and Figure-3, were investigated. Appear of new

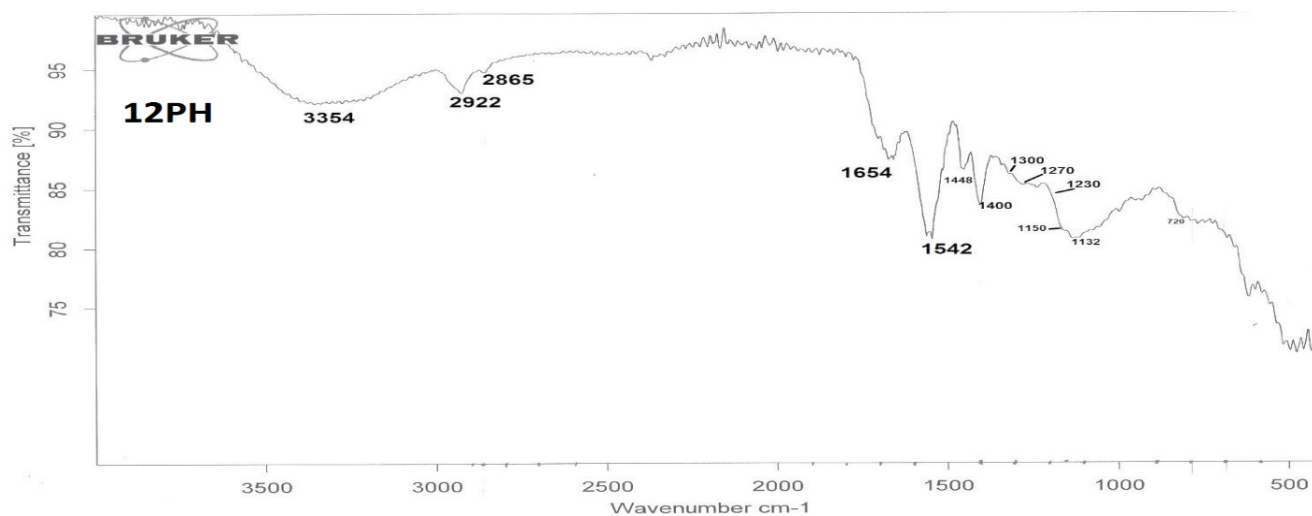
characteristic bands in produced polymers and disappear of others for the raw materials were proved the formation of new SAPs. Figure-2 has shown disappear of the characteristic band of 12CH hydrogel at 1659 cm<sup>-1</sup> of (ν(C=C)) of AA and a broad band was appeared at 3360cm<sup>-1</sup> beyond to (ν(O—H)str). In addition, a strong bands at 1720 cm<sup>-1</sup> and 1562 cm<sup>-1</sup> which represent (ν(C=O)str) and antisymm. (ν(C—O)str), respectively were recorded. According to Table-1 and Figure-3, the characteristic bands of 12PH hydrogel were almost look like 12CH hydrogel bands except those bands appeared at (720, 1100, 1152 and 1270) cm<sup>-1</sup> have been related to (—P=O) groups belong to polyphosphate anion. Moreover, superabsorbent polymers contain VP and/or AAm beside AA grafted on GA polymer their FTIR characteristic bands were studied, Table 1 and their disappeared band of (ν(C=C)) was recorded and the appearance of new bands of (ν(C—C) ring) ν(N—H)str, (ν(C—N)str) beyond to AAm or VP, respectively after polymerization were fixed.

**Table-1**  
**FTIR characteristic frequencies of main functional groups of different graft composite hydrogels**

FTIR main functional groups		Sample code					
		12CH	12PH	123CH	123PH	1234CH	1234PH
		Wave number, cm <sup>-1</sup>					
ν(C—H)str		2870\2931	2850\2923	2927	2935	2865\2942	2877\2922
ν(C—H)def		1260\1400	1230\1400	1227\1418	1229\1413	1234\1418	1230\1402
ν(C=O)str		1720	1654	1716	1660	1653	1652
ν(C—O)str	symm	—	—	1318	1322	1317	1338
	anti symm	1562	1542	1541	1550	1541	1557
ν(O—H)str		3360	3354	3350	3355	3345	3335
ν(C—OH)def		1450	1449	1440	1445	1456	1455
ν(C—O—C)str,antisymm		1163	1163	1174	1169	1169	1166
ν(C—O—C)str, symm		1070	1070	1077	1075	1030	—
ν(N—H)str		—	—	3300	3311	—	—
ν(C—N)str		—	—	1457	1451	1457	1450
ν(C—C) ring		—	—	—	—	862	860
ν(—P=O)		—	720\1100\1152\1270	—	720\1150\1266	—	730\1090\1155\1250



**Figure-2**  
 FTIR spectra of 12CH hydrogel



**Figure-3**  
 FTIR spectra of 12PH hydrogel

**Swelling Studies: Studies on swelling of chemically cross-linked SAP's:** Degree of swelling (DS) of the prepared SAP's was carried out using different concentrations of feed compositions of starting materials in order to reach the best concentration for SAP's have maximum DS. Table 2, has shown the more suitable concentrations of the starting materials used. Where 2.5% w/v of GA was suitable to graft with 7.0 mL of sodium acrylate which was important to prepare through neutralization of acrylic acid with sodium hydroxide and the best concentration was 85% w/v of acrylic acid in 8 mol/L NaOH. The study shows at 7.0 mL of 85% w/v AA:NaOH the gelation time was increased due to the increasing in the molecular weight and viscosity of produced hydrogel, and the hydrogen bonding that formed by hydrophilic units along the polymer chains beside the three dimensional compositions were sufficient for the hydrogel to reach maximum DS<sup>22</sup>.

Water absorbencies of hydrogels prepared from GA grafted with AAm or VP monomers, Table 2 have shown large depression in comparison with hydrogel grafted with sodium acrylate monomer, because of their nonionic tendency and of the steric effect of the five member ring of VP monomer, while sodium acrylate units are ionic having high hydrophilic properties. The addition of 4.0 mL of 50%w/v AAm: H<sub>2</sub>O to 7.0 mL of 85% w/v AA: NaOH was found the suitable mixture for preparation of 123CH hydrogel, Table 2. The produced hydrogel will hold both hydrophilic -COO<sup>-</sup> groups and nonionic -CONH<sub>2</sub> groups. Therefore, the maximum DS was reduced, Table 2 and the reduction was increased more when 2.0mL of 50% w/v VP: H<sub>2</sub>O was added to the previous mixture for production of 123CH hydrogel because AAm and VP monomers will impede the absorption of water molecules by sodium acrylate units.

**Table-2**  
**Feed composition of SAP's ,and their degree of swelling**

Sample code	GA (%W/V)	85% W/V AA:NaOH (mL)	50% W/V AAm:H <sub>2</sub> O (mL)	50% W/V VP:H <sub>2</sub> O (mL)	APS (%W/V)	MBA (%W/V)	SHMP (%W/V)	DS (g/g)
12CH	2.5	7.0	–	–	5.0	4.0	–	1822
123CH	2.5	7.0	4.0	–	5.0	4.0	–	595
1234CH	2.5	7.0	2.0	2.0	5.0	4.0	–	240
12PH	2.5	9.0	–	–	5.0	–	71.4	720
123PH	2.5	9.0	2.0	–	5.0	–	14.3	868
1234PH	2.5	7.0	2.0	2.0	5.0	–	28.6	486

**Hydrogel functional groups and their effects on water absorbency:** Differences in DS of prepared SAPs were due to the difference in their functional groups which are responsible for water absorbency. Hydrophilicity, polarity and electronegativity of functional groups, beside porosity, degree of cross-linking and chain length of the polymer<sup>23,24</sup>, are the main effective properties which could differentiate in water absorbency between hydrogels. Sodium acrylate has highly hydrophilic carboxylic group –COO<sup>-</sup> with high electronegativity and polarity which could physically interact with water molecules. The electrostatic repulsion of carboxylate groups can expand the polymer chains and result in high DS<sup>25</sup>. While amide group-CONH<sub>2</sub> and pyrrolidone group, beside nonionic, they are less polarity and electronegativity than carboxylate groups, so it reflect on their water absorbency. Moreover, the intermolecular hydrogen bonding between the functional groups itself will reduce significantly the hydrogen bonding with water molecules and decrease the elasticity of polymer chains. While repulsion between functional groups such as carboxylate groups which force the polymer chains to expand and hold more water molecules where their elasticity and porosity would increase.

**Studies on swelling of physically cross-linked SAP's:** Sodium hexameta polyphosphate (SHMP), the polyanion salt was used instead of N,N'-methylenebisacrylamide as physical cross-linker for preparation of the previous SAP's. The changes were done for comparison, and to improve the degree of saturation of agriculture soil will be high and its water-retention percentage will continue for a long time, and under real agriculture irrigation conditions. The complexation of hydrogels in presence of physical cross-linker was found to be simple and mild<sup>26</sup> and depend upon charge density and concentration of counter polyanions. The magnitude of electrostatic interactions between hydrogel and polyanions depends on the ionic strength of the medium, which provide opportunities to modify the electrostatic interactions to form three-dimensional network structure inside the prepared hydrogel. The high charge density of SHMP would provide strong electrostatic interactions with polyelectrolyte polymers in comparison to other types of Polyanion salts<sup>26</sup>.

Different SAP's cross-linked physically have shown, Table-2 different concentrations of SHMP depending upon their ionic moieties, so 12PH hydrogel need 71.4 % w/v SHMP because of its high ionic moieties in comparison with 123PH hydrogel which has used only 14.3% w/v SHMP because of its nonionic nature, while 1234PH hydrogel consumed 28.6% w/v of SHMP in order to reach its maximum DS which means higher than 123PH hydrogel although it is nonionic, and this is because of its pyrrolidone groups which cause steric effect and prevent the polyanion salt to extend and interact easily with polymer chains. It has been shown from Table-2, the DS of 12PH hydrogel is less than 12CH hydrogel which may because in the physical interaction a repulsion may occur between sodium carboxylate groups –COO<sup>-</sup>Na<sup>+</sup> and polyphosphate groups of polyanion SHMP. The carboxylate-SHMP polyanions repulsion will force polymer chains to extend so that the three-dimensional structure would be improved, elasticity of the polymer chains would increase, and the hydrogel with physical cross-linker became more compact. But, because of the repulsion, the polymer will lose some of its interactions with water molecules, so a decrease in its DS has been recorded.

The elevation in DS of 123pH hydrogel Table-2, in comparison with 12pH hydrogel was due to the additional amide groups which are nonionic, which will spend in holding extra molecules of water. While 1234pH hydrogel and because of its steric effect come from pyrrolidone groups, its DS decrease but still it is larger than 1234pH hydrogel, which means cross-linking has a significant effects on the polymer network structure of the hydrogel.

**Salt solution and DS of hydrogels:** It is very important to measure the DS of the prepared SAPs in salt solution because the sources of plants irrigation water are either the rains or it taken directly from rivers. Anyway moving of water through sandy soil, part of solid salts will already dissolve and reach hydrogel particles if was used. Two main divalent cations Ca<sup>+2</sup> and Mg<sup>+2</sup> are present in sandy soil, mainly in the form of calcium chloride (CaCl<sub>2</sub>) and magnesium sulphate (MgSO<sub>4</sub>) and

are either present originally in soil or they comes from outside sources such as fertilizers. The DS of different SAP's in salt solution medium was reduced significantly comparing to their values in deionized water Figure-4 and Figure-5, because of what is called screening effect<sup>27</sup>, where cations such as calcium or magnesium ions present in hydrogel swelling medium form anion-anion electrostatic repulsion, which lead to depress in the osmotic pressure (ionic pressure) different between the hydrogel network structure and the external solution. Also the penetration of counterions ( $\text{Ca}^{+2}$  or  $\text{Mg}^{+2}$ ) into polymeric network increase their screening effect on anionic group ( $-\text{COO}^-$ ). In addition, screening effect can form an intramolecular and intermolecular complex between the anionic group ( $-\text{COO}^-$ ) with the divalent anion ( $\text{Ca}^{+2}$  or  $\text{Mg}^{+2}$ ) and as a result, water absorbency will became lower with increasing of external salt concentration<sup>28</sup>. Chemically cross-linked hydrogels have shown Figure-4 and Figure-5 high depression in their DS as the concentrations of salt solution increase, especially in  $\text{CaCl}_2$  salt solution because

$\text{Mg}^{+2}$  ion is smaller and has less radius than  $\text{Ca}^{+2}$  ion, although they have the same valence, and it was proved that less radius cation of the same valence, the more the water absorption capacity ( $\text{Ca}^{+2} < \text{Mg}^{+2}$ ) because large size cations like  $\text{Ca}^{+2}$  cannot inter inside the hydrogel and as a result will remain inside swelling medium and keep its screening effect active on hydrogel functional groups<sup>29</sup>. However, physically cross-linked hydrogels Figure-4 and Figure-5 have shown more resisting to the screening effect caused by ( $\text{Ca}^{+2}$  or  $\text{Mg}^{+2}$ ) cations because they could not able to form a shield against the repulsive intra-chain electrostatic forces<sup>30</sup>. The extra anion charges present on SHMP cross-linker chains inside the hydrogel network would prevent such type of shield, but at higher  $\text{CaCl}_2$  concentration (around 1000 ppm), the osmotic pressure would reduce because of the balance in the concentration of the ions inside the hydrogel and its swelling medium, and as a result the DS of the physically cross-linked hydrogels would decreased.

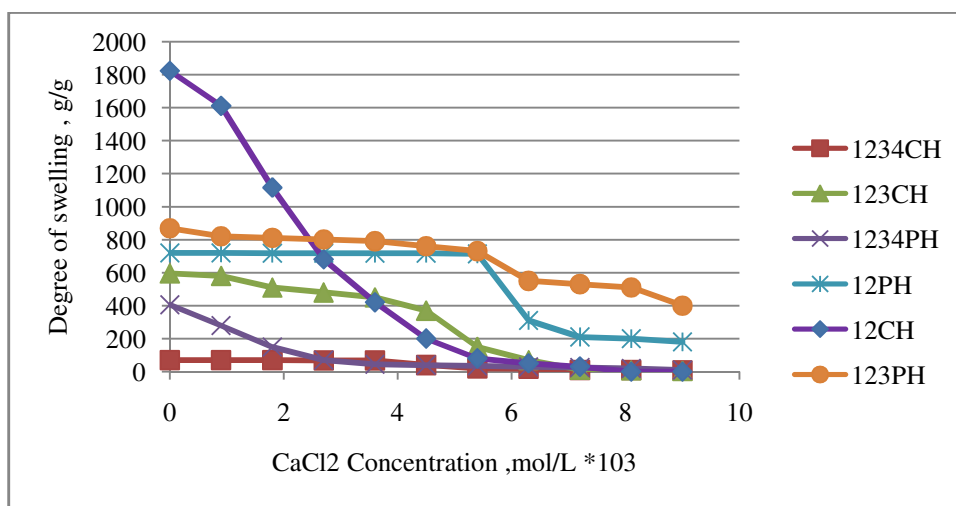


Figure-4

Effect of  $\text{CaCl}_2$  different concentrations on degree of swelling of different prepared hydrogels

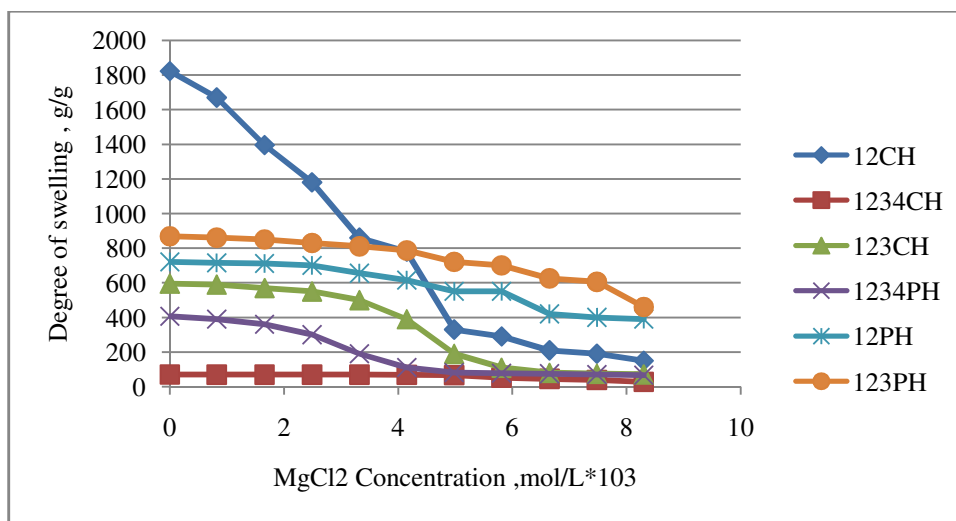


Figure-5

Effect of  $\text{MgSO}_4$  different concentrations on degree of swelling of different prepared hydrogels

**River water and its effect on swelling of hydrogel:** The total hardness of the river water sample was measured and its average was recorded around 400 mg/L (400 ppm). A comparison study was done for some SAP's samples Figure-6, for their DS in deionized water and river water. The 400 ppm hardness in swelling medium could form a shield against the repulsive intra-chain electrostatic forces in chemically cross-linked hydrogels, especially those have hydrophilic functional groups and depending on their hydrophilicity in water absorbency, where river water cations could form a shield and a highly reduction in their DS was observed. Whereas, samples with less hydrophilicity like 123CH or 1234CH, are less effected with river water cations because already are nonionic. However, physically cross-linked SAP's and because of their SHMP polyanions have shown Fig 6, almost no change in their DS with cations of river water, especially for the hydrogel sample 123PH Where no change in its DS were recorded due to its high density of anions which could neutralize the river water cations and no screening effect could reduce its water absorbency.

**Effect of pH medium on swelling of hydrogel:** Hydrogels are polyelectrolyte materials mainly depend in their swelling on ionization or protonation of their functional groups. So that, the pH medium where SAP is swell has strong influence on the reply of hydrogel functional groups. Both hydrogels cross-linked physically or chemically have shown in Figure-7 their maximum DS in swelling solution at (pH7), but each has its own reason. Chemical cross-linked samples at lower pH swelling solution (pH6 and pH5) their carboxylate anions along the hydrogel chains have shown highly protonation which result a diminishment of the anion-anion repulsion forces. Therefore, their DS was decreased as the pH decrease. Moreover, at external swelling pH higher than 7, the sodium ion-induced charge screening effect would occur, which shield the carboxylate anions and thus interfered with the electrostatic repulsion<sup>23</sup> and as a result the DS of the hydrogels would reduce at pH 8. Physical cross-linked samples have shown variations Figure-7, in their degree of ionization in different pH solution with more trend than chemical cross-linked hydrogels. Sodium hexameta polyphosphate SHMP is a polyanion salt, its degree of ionization decrease as the pH medium decrease<sup>26</sup>. Therefore, at (pH7) the degree of ionization of both hydrogel and SHMP was maximum with a best three-dimensional network have been formed and finally shown high water absorbency. Above (pH7), the increase in sodium ions will induce electrostatic screening effect of the counterions on hydrogel functional groups which reduce the electrostatic interactions between hydrogel and SHMP anions. Therefore, water absorbency of the hydrogel would reduce.

**Saturation degree of Sandy Soil mixed hydrogel:** SAP's have been mixed with sandy soil in low percentage, in order to increase water holding-capacity and decrease irrigation intervals<sup>31</sup>. Mixing SAP with sandy soil and then start irrigation, the water moisture enters into the internal network easily, and forms a water-blocking layer between soil particles. When the

molecular chain swelled under the three-dimensional cross-linked structure, which could inhibit moisture from moving either from soil surface to the atmosphere or to rock layer of slops, but make it moving horizontally, or to the place that had little SAP<sup>32</sup>. It was found through experiments, 1.0% w/w SAP mixed with sandy soil was the suitable percentage to reach the aim of increasing the soil saturation degree to maximum. Physical cross-linked hydrogels mixed in 1.0%w/w with sandy soil have shown Figure-8 and using Equation-2, the highest degree of saturation where rainwater was used in irrigation. Generally, and because physical cross-linked hydrogels could hold large quantities of water molecules for their three-dimensional network, and because these hydrogels have shown less effects with salt solutions, hardness of irrigation water, pH of swelling medium and others, and because of their electrolytic interactions, they could clearly increase the water-holding capacity of the sandy soil and store rainwater there efficiently. Acrylamide groups or pyrrolidone groups and because they are nonionic groups, they have shown less effects by external salts solution present in Sandy soil. In addition, pyrrolidone groups could built good network structure which can holding high amount of rainwater.

**SAP mixed sandy soil and their water-retention behavior:** The absorption of superabsorbent polymers for a large quantity of water in comparison with general water absorbing materials is not its only advantage, but even can save the absorbed water with no remove even under some pressure<sup>33</sup>. And according to a foresaid, the SAP activities were investigated in agriculture field, where 1.0% w/w of two selected hydrogel samples (12CH and 12pH) has been mixed with sandy soil. The prepared sample in paper cup that contain 200g sandy soil and 2g hydrogel (represent 1.0% w/w) was irrigated with 100mL rainwater. Same procedure was applied on reference sample contain no hydrogel. Water-retention percentage (WR%), according to Equation-3 was measured daily for all samples which were incubated at suitable temperature and humidity, and their results were drawn in Figure-9. Mixing of prepared SAP with soil sample could clearly increase the water-retention for a long time. Where in, the reference sample has shown WR%= 6.0% after 10<sup>th</sup> days and WR%= zero after 20<sup>th</sup> days, while those samples have soil mixed with SAP have shown WR%= 40 after 10<sup>th</sup> day and WR%= 14 after 20<sup>th</sup> day. Moreover, Water-retention by soil with hydrogel sample and after 30 days seems to be wet, and its WR%= 4 and especially in case of physical cross-linked hydrogel sample. Therefore, soil sample contain 12PH sample has shown higher WR% at certain time period in comparison with 12CH hydrogel soil sample Figure-9, because 12PH hydrogel was shown less effects to its surrounding conditions as 12CH hydrogel such as salt solution and pH of swelling medium. Furthermore, it was seen that the sandy soil without SAP was rigid and cracked after some time, whereas the soil in presence of SAP retained with its configuration and seems to be in granular structure where this was also seen by others<sup>34</sup>. Finally the addition of SAP with suitable percentages to soil samples could improve the agriculture properties of soil



with high water absorbency, water-retention, and even moisture preservation capacity. In addition, physical cross-linked hydrogel and because of their ionic structures and due to their electrostatic interactions, they are less damage by different

surrounding conditions especially the external ions that came from the soil itself or the fertilizers or from hard water used during irrigation.

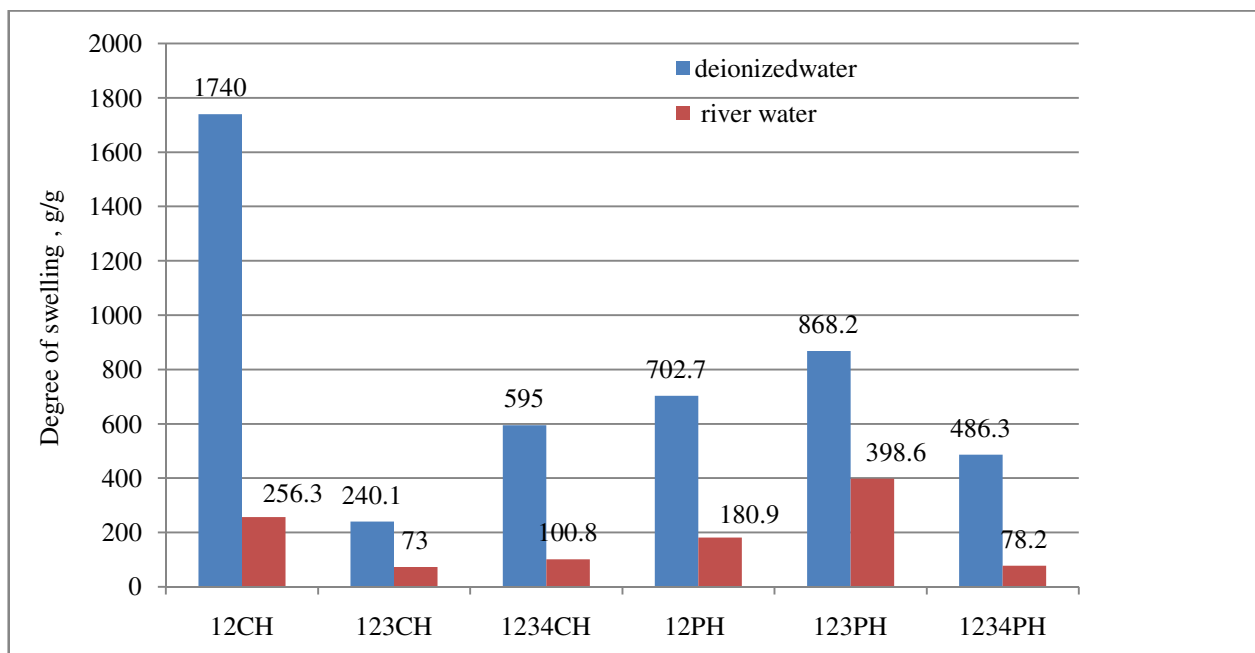


Figure-6

Comparison study in maximum degree of swelling of different prepared hydrogels carried out in deionized water and river water (around 400 ppm hardness) swelling medium

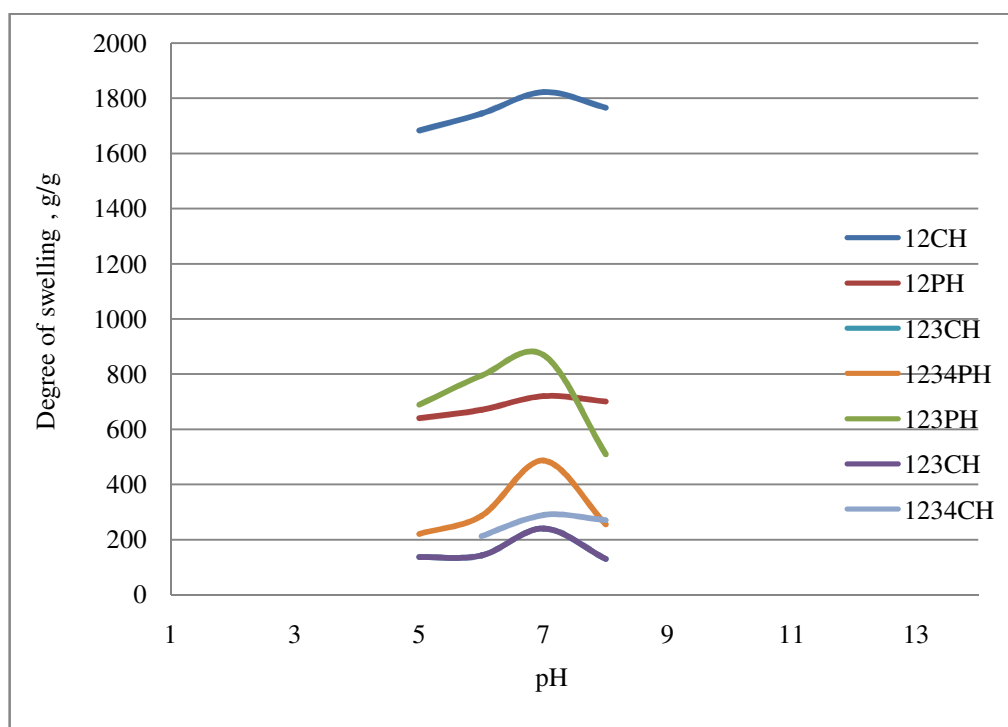


Figure-7

Effect of some external pH solutions on degree of swelling of different prepared hydrogels

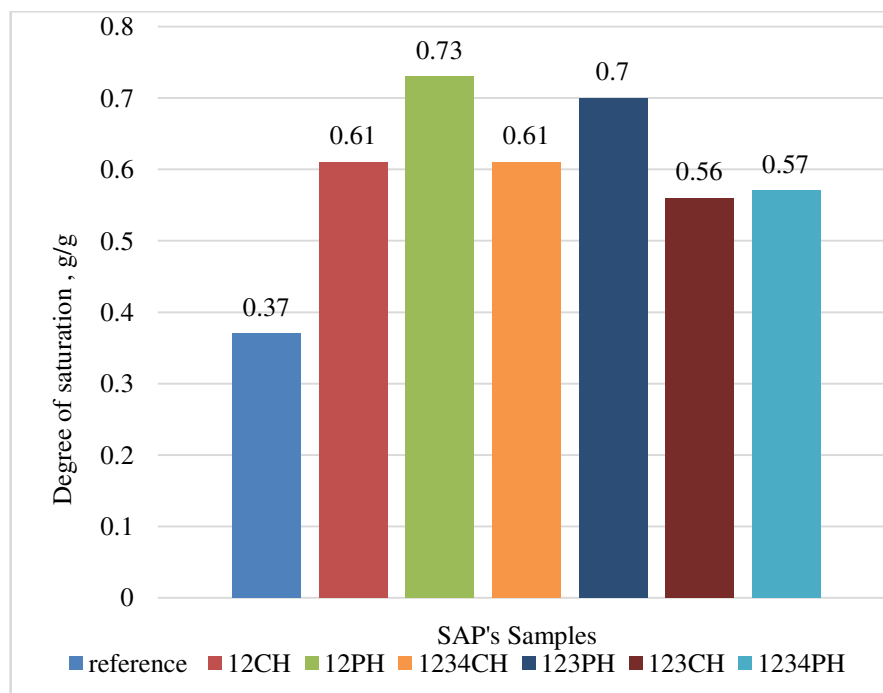


Figure-8

Effect of hydrogel composition structure that mixed with sandy soil on its degree of saturation using rainwater

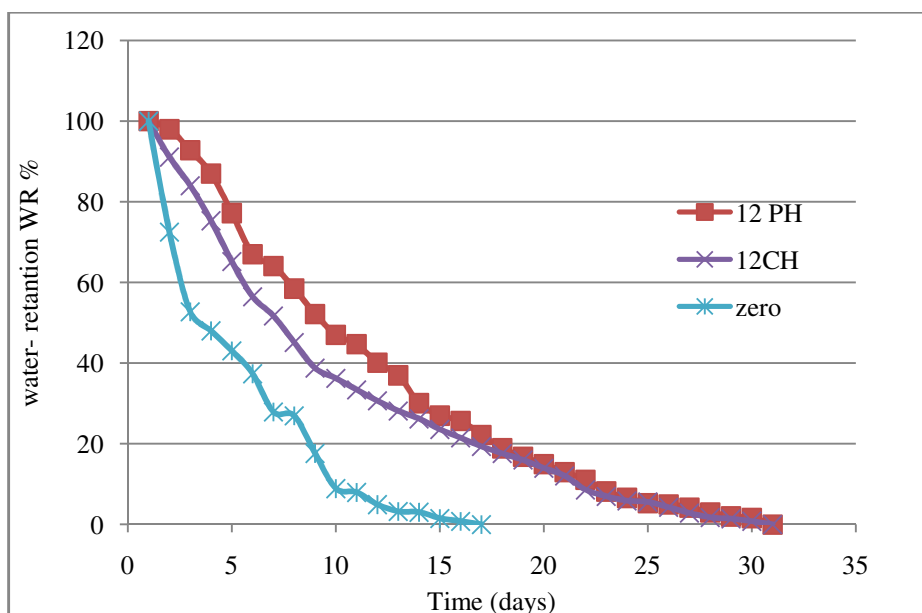


Figure-9

Effect of superabsorbent polymers mixed with sandy soil on its water-retention percentage with time (days), using (GA-g-AA) hydrogels cross-linked chemically and physically beside an pure soil sample

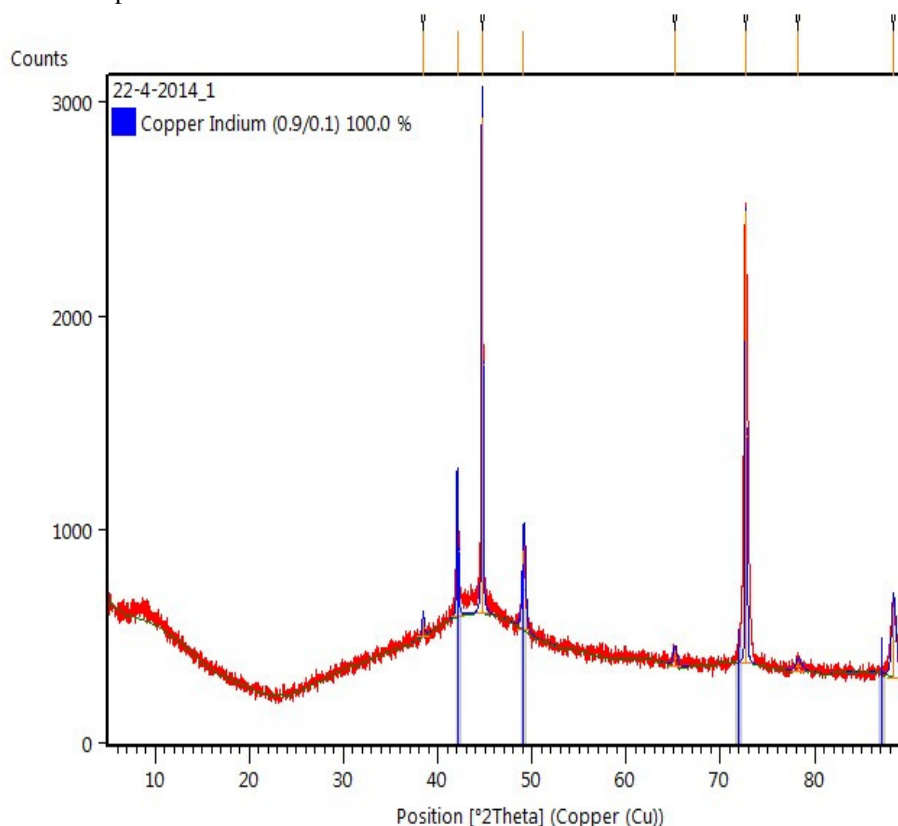
**Characterization studies: X-ray analysis:** The XRD patterns of 12PH sample was characterized, because of its type of cross-linker (SHMP) which was used for the first time where no literatures have been mentioned before. Figure-10, has shown the scattering curve at a d-spacing of 2.14086 ( $2\theta=42.177$ ) appear as a prominent peak corresponding to the sodium

acrylate polymer chains grafted on the main polymer chains of gum arabic. Moreover, GA appear also as a prominent peak at a d-spacing of 1.85402 ( $2\theta=49.098$ ). Whereas, sodium hexameta polyphosphate peak was occurred at a d-spacing of 1.31093 ( $2\theta=71.973$ ) which is prominent and intense peak. The XRD pattern, Fig 10 has shown the peaks are sharp and intense,

which means the physical cross-linker could arrange the hydrogel in a good three-dimensional structure. The fourth prominent peak occurred at a d-spacing of 1.11798 ( $2\theta=87.104$ ), Figure-10, is to match with sodium ions present in the hydrogel came from sodium acrylate and SHMP. The final results of XRD pattern prove that the 12PH sample was arranged in an excellent morphological structure have good three-dimensional network.

**SEM analysis:** SEM images and surface morphology of (GA-g-AA) hydrogel cross-linked chemically (12CH) and physically (12PH) samples were investigated and their quantitative elemental composition percentages were determined. The SEM image of 12CH hydrogel Figure-11A, B, C have shown clearly the surface morphologies of the hydrogel, where Figure-11A, shows a relatively undulant and coarse surface with some holes. Therefore, it is suitable for penetration of water into the

polymeric structure, and as a result it is useful for more water absorbency. At higher magnification, Figure-11B, the SEM image has shown the undulant and coarse surface seems to be not deep and with less porosity which may because of the chemical cross-linking of the polymer chains that lead to dense and tighter surface. However SEM image of dry 12CH sample, Figure-11C, has shown broken particles and seems to be hard, dense, smooth and tight surface with no uniform shapes. Beside the images, SEM gave quantitative elemental composition percentages of 12CH hydrogel sample, where the carbon weight % of the sample was 50, and oxygen weight % and sodium weigh % were 40 and 10, respectively. The quantitative elemental composition percentages are good evidence for hydrogel is pure and mainly consist of GA and sodium acrylate, beside the oxygen weight % of 40 means the hydrogel have a lot of functional groups with high electronegative element.



NO	Intensity (%)	D-spacing (Å)	2 theta(°)	Hkl
1	100	2.14086	42.177	111
2	45.9	1.85402	49.098	2
3	23.8	1.31093	71.973	22
4	25.6	1.11798	87.104	113

**Figure-10**  
 XRD diffractogram of (GA-g-AA) hydrogel cross-linked physically with SHMP

The SEM images of 12PH hydrogel have shown, Figure-12A, B, C the surface morphologies of the highly porous hydrogel, where Figure-12A has clear the rough surface of the hydrogel with high numbers and uniform pores were proved the fast swelling properties of 12PH hydrogel which related to its absorption not by diffusion process but through capillary mechanism. The whitening regions in Figure-12A have shown the irregularity in the hydrogel surface and its folds. The SEM image recorded for 12PH hydrogel surface Figure-12B, has shown the large size pores with their deep cavities and they spread uniformly along whole surface. Whereas Figure-12C has shown highly uneven folds contain inside and in between folds which means the hydrogel could be present in elastic form<sup>35</sup>, with the help of its ability to form the three-dimensional structure easily with SHMP cross-linker. In addition, the quantitative elemental composition percentages of 12PH hydrogel sample that concluded from SEM as weight % are, C = 37%, O = 46%, Na = 10% and P = 7%, mean 12PH hydrogel is very pure sample. Beside the oxygen weight % present in the hydrogel is in a highest percentage which means 12PH sample has more hydrophilic functional groups in comparison with 12CH of same structure. And this is may be because of its some functional groups have been engaged with chemical cross-linking process. 7% phosphorous present in 12PH hydrogel means sodium hexameta polyphosphate salt became part of the three-dimensional structure of the hydrogel and its physical electrostatic interactions between its chains are fixed and strong.

**Thermal analysis:** Differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA) of prepared hydrogels were studied and some of their thermogram curves were cleared. Pure gum arabic thermal character has shown maximum decomposition temperature at  $T_{max} = 310^{\circ}\text{C}$  and the gum Arabic was decomposed completely at  $500^{\circ}\text{C}$ , and its DSC curve has

shown the gum is semicrystalline hydrogel close to amorphous natural polymer. Gum arabic grafted with sodium acrylate and cross-linked chemically would produce 12CH hydrogel, which has shown its DSC-TGA in Figure-13A where its  $T_{max} = 370^{\circ}\text{C}$  means thermally gum arabic become more stable after grafting and only 46% of the polymer was decomposed at  $500^{\circ}\text{C}$ . The DSC curve of 12CH hydrogel, Figure-13A has shown an increase in its crystallinity after grafting. The physical cross-linked hydrogel (12PH) has shown completely different thermal characteristic behavior. Where Figure 13B has shown a depression in  $T_{max}$  of 12Ph hydrogel on TGA curve with a sharp decomposition at  $T_{max} = 203^{\circ}\text{C}$  and the hydrogel was decomposed completely at its  $T_{max}$ . The DSC curve, Figure 13B has shown the hydrogel was amorphous. But has shown also, when the hydrogel decomposed completely, the cross-linker sodium hexameta polyphosphate remain as a semicrystalline salt in DSC curve and appear at  $410^{\circ}\text{C}$ . Anyway, thermal stability of physically cross-linked hydrogel was lower than that of chemically cross-linked, and more amorphous, which was seen through SEM study. The physical cross-linked hydrogels prepared from grafting of GA with AA and AAm (123PH) hydrogel or with AA and AAm and VP (1234PH) hydrogel were also studied and their DSC-TGA thermogram Figure-14A and Figure-14B, respectively have shown hydrogels with high thermal stability in comparison with 12PH hydrogel due to the presence of N-vinyl pyrrolidone and/or acrylamide chains. While the DSC curves in Figures-14A and Figure-14B have shown 123PH hydrogel is highly amorphous and 1234PH hydrogel is highly crystalline, respectively and these explain why 123PH hydrogel has high water absorbency than 1234PH and even than 12PH hydrogel. Therefore, hydrogel with high thermal stability and amorphousity was the best in water absorbency.

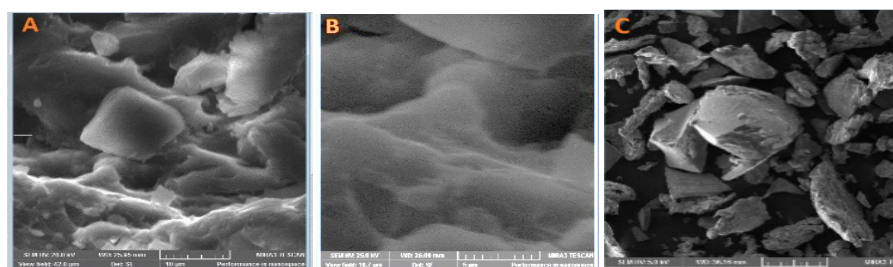


Figure-11

SEM images of 12CH hydrogels, where (A) surface morphology with undulant and coarse surface with some holes, (B) dense and tight surface, and (C) hard and broken particles

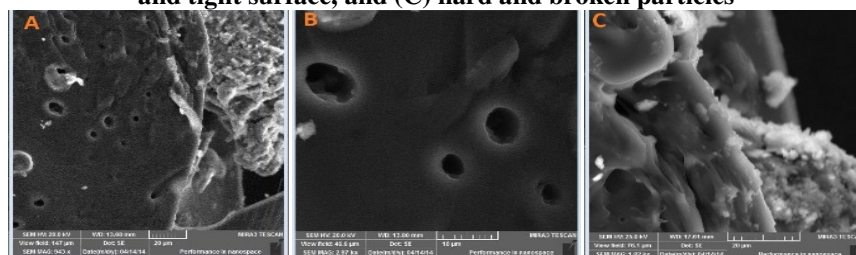
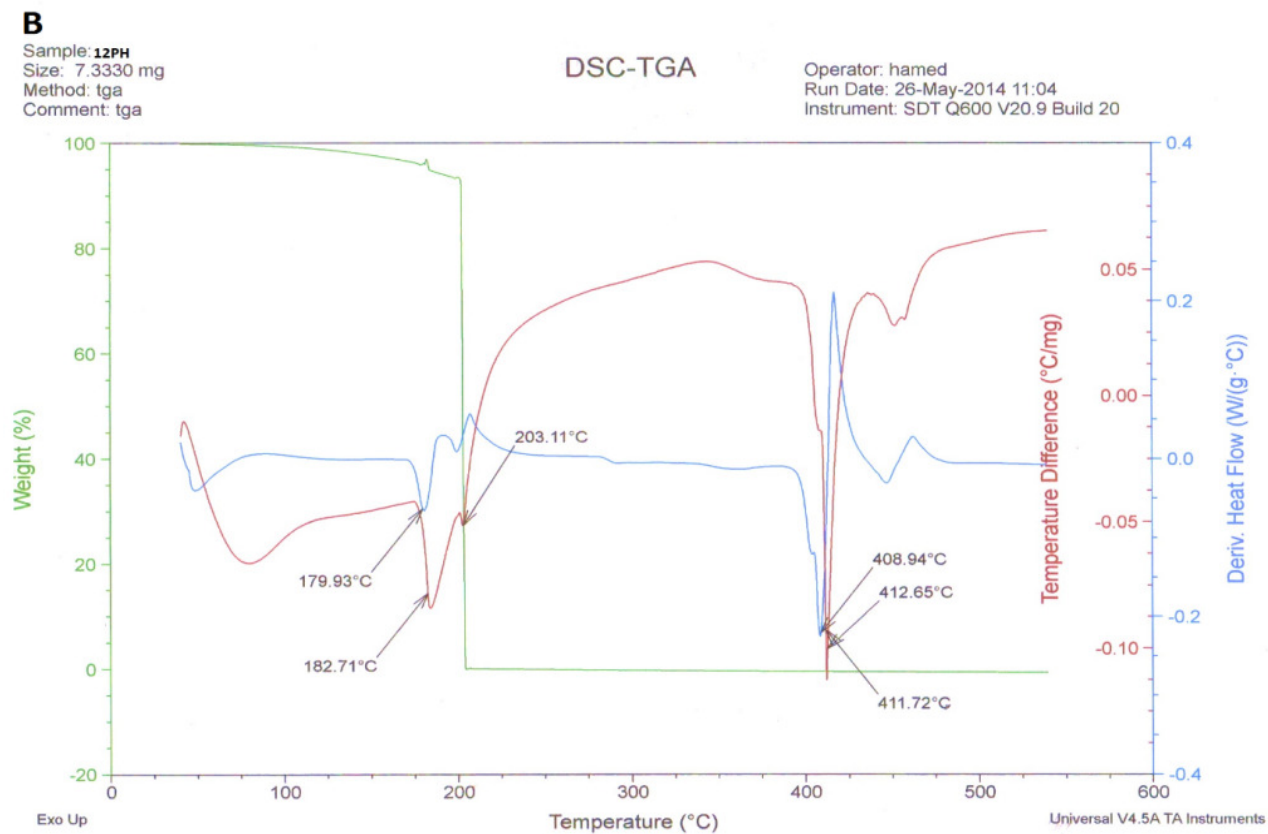
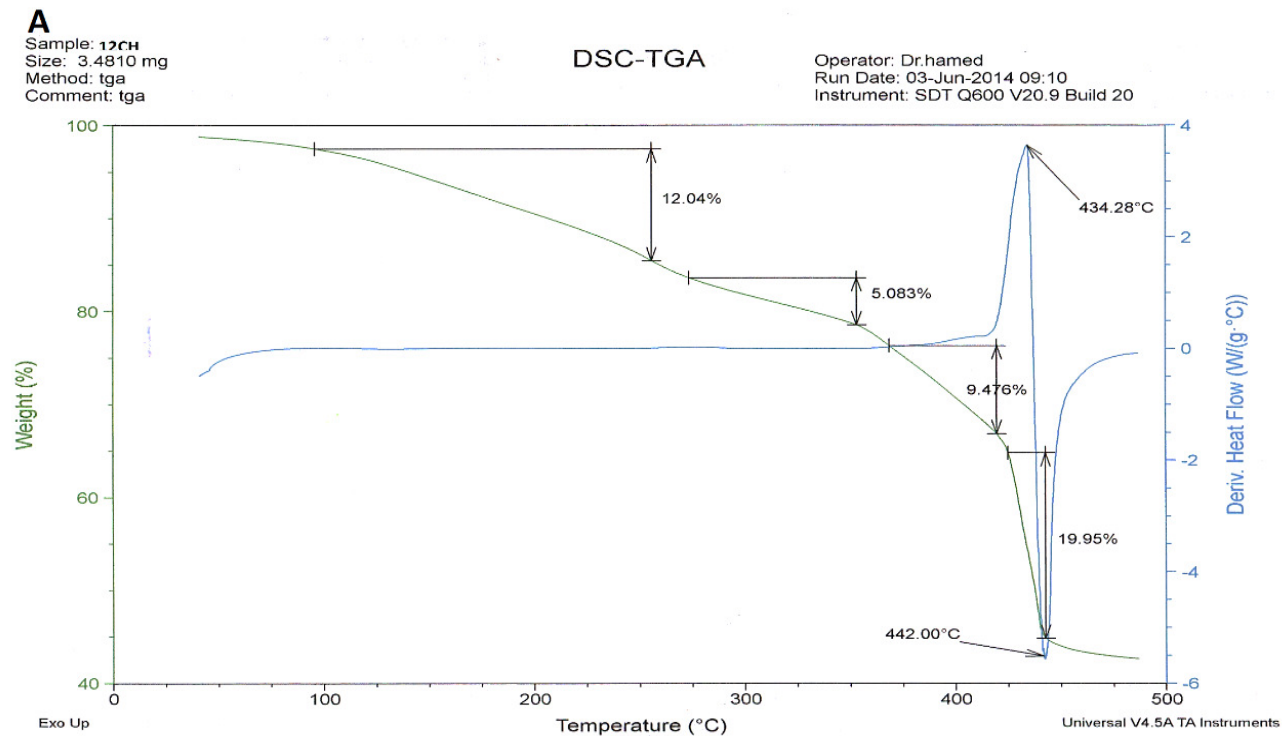
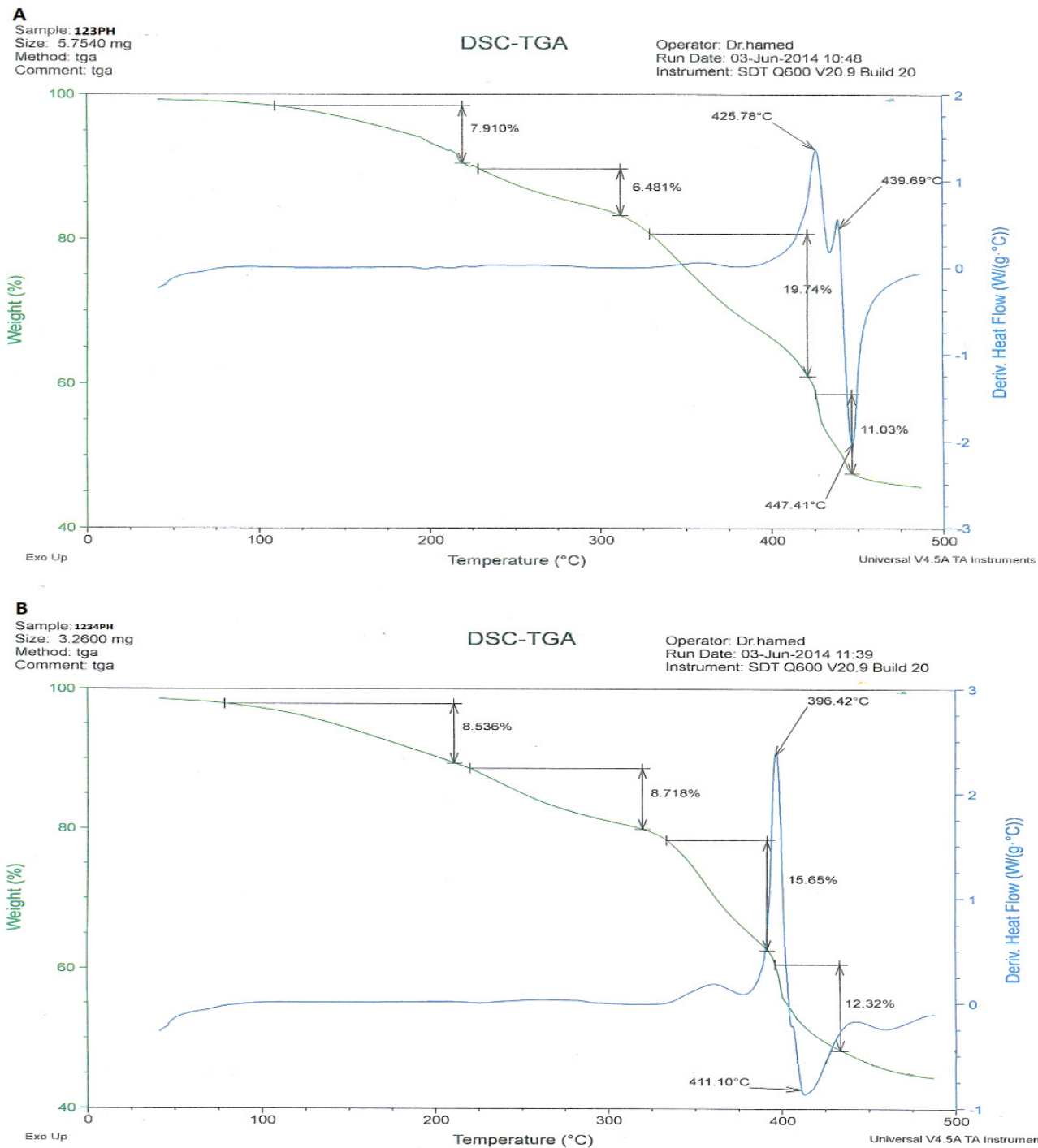


Figure-12

SEM images of 12PH hydrogels, where (A) highly uniform porosity with irregular and fold surface, (B) deep cavities with large size, and (C) uneven folds with inside pores



**Figure-13**  
DSC -TGA thermal-diagram of, (A) 12CH and (B) 12PH, hydrogels



**Figure-14**  
 DSC –TGA thermal-diagram of, (A) 123PH and (B) 1234PH, hydrogels

### Conclusion

Physical cross-linking SAP's especially if they are nonionic in nature, are more suitable materials help in agriculture irrigation of plant germinate in arid and desiccated regions. Gum arabic, the neutral nonionic polysaccharide was modified by grafting

with synthetic monomer like sodium acrylate, N-vinyl pyrrolidone and/or acrylamide. The prepared SAP's were cross-linked chemically like MBA or physically like SHMP. The water absorbance character of the hydrogels is different due to the difference in their hydrophilicity, three-dimensional networks and their morphological structures, type of interactions

between their chains and the mole fractions of raw materials used in their polymerization process. The degree of swelling of SAP's varied according to the variable swelling medium conditions like, PH, present of salt such as  $\text{CaCl}_2$  or  $\text{MgSO}_4$ , hardness of irrigation water, where those different elements have a significant effects on water absorbency of SAP's. The prepared SAP's were mixed with soil in order to keep the later wet for a long period of time during agriculture. Therefore, the most important points in agriculture are to increase the saturation degree of soil with water and to keep water-retention percentage of soil for a long period of time. Physical cross-linked hydrogels and due to their electrostatic interactions and because of their perfect three-dimensional network are more suitable SAP's and could be use in agriculture. Different types of salts either present in the soil or deposit from irrigating water or fertilizer decomposition. Salt cations will compete with the ionized functional groups of chemically cross-linked hydrogels in their interactions which are responsible for hydrogen bonding. While part of the polyanions of the cross-linker SHMP will engage with salt cations and other hydrogel function groups have good chance for more hydrogen bonding. The XRD clear that physical cross-linker could improve the three-dimensional structure of the hydrogels. SEM technology provide information about the quantitative elemental compositions of the hydrogels and shown good images about porosity, deep cavities and uneven fold in physical cross-linked hydrogels, whereas not deep undulant and coarse surface with less porosity in chemical cross-linked hydrogels. DSC-TGA studies have shown crystalline structure with high decomposition temperature with chemical cross-linked hydrogel facing amorphous and low decomposition temperature in physical cross-linked hydrogels. SAP's cross-linked physically have shown perfect thermal and mechanical properties with less damage by different surrounding conditions and finally have excellent water absorbency, water-retention and moisture preservation capacity.

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