SYNTHESIS AND SWELLING PROPERTIES OF POLY[ACRYLAMIDE-*co*-ACRYLIC ACID] SUPERABSORBENTS OBTAINED BY ELECTRON BEAM IRRADIATION

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The aim of this study is to investigate the gel fraction, sol fraction, water absorbency and crosslink density of superabsorbents based on polyacrylamide/acrylic acid. Superabsorbents were prepared by free radical co-polymerization in aqueous solution of acrylamide with acrylic acid and different concentration of initiator at room temperature (25°C). Samples were subjected to electron beam treatment with doses ranging between 3 and 4.5 kGy.

Keywords: copolymerization, acrylamide, acrylic acid, superabsorbent, electron beam.

INTRODUCTION

Superabsorbent polymers were defined as three-dimensional networks of hydrophilic polymers that can absorb and retain a significant amount of water. In agriculture, superabsorbent polymers are especially used for soil conditioning and to increase the efficiency of fertilization. Thus, this class of materials has been developed to improve the physical properties of soils by: increasing water holding capacity and efficiency of its use, increasing soil permeability and stopping their erosion, decreasing the frequency of irrigation, reducing the tendency to form crust, increasing agricultural performance especially on unstructured soils, reducing fertilizer losses and fostering their uptake by plants (Baker *et al.*, 1994; Mihailescu *et al.*, 2004; Mihailescu *et al.*, 2007; Seybold, 1994;). Three main types of hydrogels (synthetic soil conditioners) have so far been developed as agricultural polymers: (1) starch-graft copolymers obtained by graft polymerization of polyacrylonitrile onto starch followed by saponification of the acrylonitrile units (2) cross-linked polyacrylates (3) cross-linked polyacrylamides and cross-linked acrylamide-acrylate copolymers (Ekebafe *et al.*, 2011). Most of the hydrogels marketed for agriculture come from the latter group as they are claimed to remain active for a much longer time (Ekebafe *et al.*, 2011). Cross-linked polyacrylamides hold up to 400 times their weight in water and release 95% of the water retained within the granule to growing plants (Ekebafe *et al.*, 2011). Radiation initiation of chemical reactions has been increasingly used for creation of novel hydrogels. A radiation technique is more preferable than a chemical one, because of the advantage to control gently the level of crosslinking by variation of the absorbed dose. This method offers unique advantages for the synthesis of new and modification of existing materials: it is a simple, additive-free process at all temperatures, reactions such as polymerization, crosslinking and grafting can easily be controlled, and the treatment can be limited to a specific area (Karadag *et al.*, 2004). Recent articles reports a series of methods for obtaining these superabsorbent copolymers with a view to enhance their absorbency, gel strength, and absorption rate. Hekmat *et al.* have synthesized a

hydrogels by using acrylamide free radical, potassium acrylate, and linear polyvinyl alcohol (Hekmat *et al.*, 2009). Ammonium nitrate was used (loaded) in the hydrogel as the fertiliser. Sayeda M. Ibrahim et all. (Sayeda *et al.*, 2007) obtained a superabsorbent hydrogels based on crosslinked carboxymethyl cellulose polymer and acrylamide monomer by electron-beam irradiation.

The aim of this study is to investigate the swelling properties of polyacrylamide/ acrylic acid hydrogels. Hydrogels have been prepared by electron beam irradiation at room temperature (25°C). The influence of absorbed dose on gel fraction and swelling behavior was investigated.

EXPERIMENTAL

Materials

In order to obtain the hydrogels, the following materials (Table 1) have been used: acrylamide (molar mass 71.08 g mol^{-1}; density 1.13 g/cm^3); acrylic acid (molar mass 72.06 g mol^{-1}; density 1.051 g/mL) and potassium persulfate (molar mass 270.322 g mol^{-1}; density 2.477 g/cm^3) - serves as initiator in the copolymerization process. All materials were procured from E-Merck, Germany.

Table 1. Used monomers in preparation of hydrogels

	Formula	Abbreviations
Acrylamide	H_2C=CH-$CONH_2$	AMD
Acrylic acid	H_2C=CH-COOH	AA
Potassium persulfate	$K_2S_2O_8$	PP

Preparation and Irradiation of the Samples

Series of hydrogels having different compositions of AMD and AA were synthesized as given in Table 2.

Table 2. Synthesis details of poly(acrylamide-co-acrylic acid) hydrogels

Sample code	AMD (mol/l)	AA (mol/l)	$K_2S_2O_8$ (mol/l)	Dose (kGy)
H_{1-1}	5	0.5	0.7×10^{-3}	3
H_{1-2}				3.5
H_{1-3}				4
H_{1-4}				4.5
H_{2-1}	5	0.5	3.5×10^{-3}	3
H_{2-2}				3.5
H_{2-3}				4
H_{2-4}				4.5
H_{3-1}	5	0.5	7×10^{-3}	3
H_{3-2}				3.5
H_{3-3}				4
H_{3-4}				4.5

Experimental Installation and Sample Irradiation

Experiments were carried out with an experimental installation consisting mainly of the following units: an electron linear accelerator (ALIN-10) of 6.23 MeV energy and

75 mA peak current of the electron beam and an irradiation chamber containing the samples of monomer solution. The ALIN 10 is a travelling-wave type, operating at a wavelength of 10 cm and having 164 W maximum output power. The optimum values of the EB peak current I_{EB} and EB energy E_{EB} to produce maximum output power P_{EB} for a fixed pulse duration τ_{EB} and repetition frequency f_{EB} are as follows: E_{EB} = 6.23 MeV, I_{EB} =75 mA, P_{EB} = 164 W (f_{EB} = 100 Hz, τ_{EB} = 3.5 μs). The EB effects are related to the absorbed dose (D) expressed in Gray or J kg^{-1} and absorbed dose rate (D*) expressed in Gy s^{-1} or J kg^{-1} s^{-1}. Electron beam dose rate was fixed at 2.4 kGy/min in order to accumulate doses between 3-4.5 kGy and samples were irradiated in atmospheric conditions and at room temperature of 25°C.

RESULTS AND DISCUSSION

In the present study, the hydrogels have been obtained by maintaining a fixed concentration of AMD and AA in the reaction mixture and varying only the concentrations of $K_2S_2O_8$ (as crosslinker) and the absorbed dose. The following parameters were determined: the soluble fraction, the gel fraction, the water absorbency and the crosslinking density.

Gel Fraction and Sol Fraction

Samples of the prepared hydrogels were accurately weighed (W_0), extracted with distilled water and then dried in a vacuum oven at 80°C to a constant weight (W_1). The soluble fraction was calculated according to the following equations (Nizam *et al.*, 2007):

$$Sol\_fraction(\%) = \frac{W_0 - W_1}{W_0} \times 100 \quad (1)$$

$$Gel\_fraction(\%) = 100 - Sol\_fraction \quad (2)$$

where W_0 is the initial weight of dried sample and W_1 is the weight of sample after extraction with water and dried.

The results presented in Figures 1 and 2 show that when both EB dose and initiator concentration increase, there is a decrease of soluble fraction and an increase of gel fraction (crosslinked polymer content).

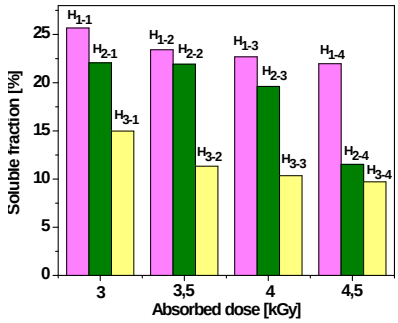

Figure 1. Soluble fraction versus absorbed dose and PP concentration

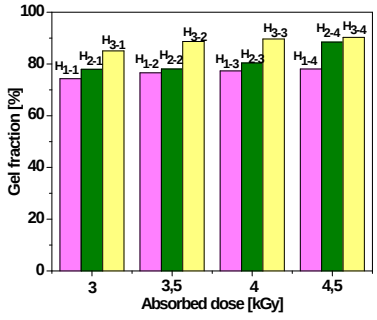

Figure 2. Gel fraction versus absorbed dose and PP concentration

The highest values for soluble fraction and gel fraction were obtained for the blends with the concentration of 7 x 10^{-3} PP and irradiated at 4.5 kGy. The addition of initiator significantly increases gel fraction. Thus, in an irradiation cure system, the gel content and soluble fraction of samples increases with increase in irradiation dose. This is due to the formation of a three-dimensional network structure.

Water Absorbency

The swelling measurements of the copolymer were carried out in water at room temperature. Two hundred grams of distilled water was added to 0.1 g of the dry copolymer in a 400 cm^3 glass beaker covered with a glass lid. The polymer was allowed to swell for 24 h. The fully swollen gel was then separated from the unabsorbed water by filtering it through a 100-mesh sieve aluminum screen for 2 h at room temperature and the swollen copolymer gel was then weighed (Yiamsawas *et al.*, 2007). The water absorbency was calculated as shown below:

$$Water\_absorbency(Q) = \frac{W_2 - W_0}{W_0} \quad (3)$$

where W_0 is the weight of the dry polymer (g) and W_2 is the weight of the water swollen gel (g).

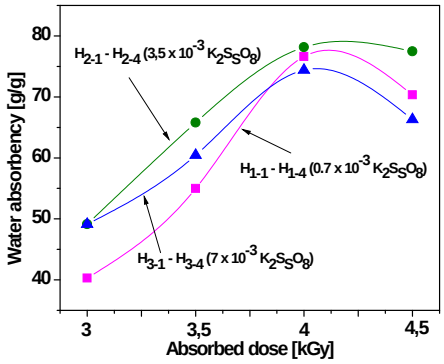

Figure 3. Water absorbency versus absorbed dose and PP concentration

The results on water absorbency of the copolymers synthesized by electron beam irradiation with various concentration of PP are shown in Figure 3. At high initiator concentrations, more crosslinks can be formed to give rigid chains that reduce the swelling of the gel. More than that, the absorption of water depends on the irradiation dose at which the samples have been obtained. It was found that maximum water absorption occurs for the samples obtained with 4 kGy. For irradiation with upper doses the absorption of water decreases, because in addition to the crosslinking reactions degradation reactions occur.

Crosslinking Density

For a polymer network, crosslinking densities of the copolymer were determined using the Flory–Rehner theory (Yiamsawas *et al.*, 2007) as follows:

$$M_C = -V_1 d_P \frac{\nu_S^{1/3} - \nu_S/2}{\ln(1-\nu_S) + \nu_S + \chi \nu_S^2} \quad (4)$$

where: M_C is the number-average molar mass of the chain between crosslinks; V_1 is the molar volume of the solvent, in this case water = 18 cm^3 mol^{-1}; d_P is the polymer density (g cm^{-3}); υ_S is the volume fraction of the polymer in the swollen gel (cm^3) and is equal to 1/S; χ is the Flory–Huggins interaction parameter between the solvent and the polymer. The value χ was taken from the literature (Yiamsawas *et al.*, 2007; Ding *et al.*, 1991; Karadag *et al.*, 1997) as follows:

$$\chi = 0.431 - 0.311\nu_S - 0.036\nu_S^2 \quad (5)$$

To determine the equilibrium volume swelling (S), it is necessary to place a sample of known density into water until mass measurements indicate the cessation of the uptaken liquid by the polymer (Yiamsawas *et al.*, 2007). If no extractable is present and all the imbibed solvent causes swelling, the volume swelling, S, is given by:

$$S = \frac{(W_2 - W_0)/d_S}{W_0/d_P} \quad (6)$$

where W_0 and W_2 are the same parameters defined earlier, d_S and d_P are the densities of water and polymer, respectively.

Here, the crosslink density, *q*, is defined as a mole fraction of the crosslink units.

$$q = \frac{M_0}{M_C} \quad (7)$$

where Mo is the molecular weight of the polymer repeating unit and is calculated using the relation (Karadag *et al.*, 1997).

$$M_0 = \frac{(m_1 \times M_1) + (m_2 \times M_2) + (m_3 \times M_3)}{m_1 + m_2 + m_3} \quad (8)$$

where m_{AMD}, m_{AA} and m_{PP} are the mass in g of acrylamide, acrylic acid and the initiator, and M_{AMD}, M_{AA} and M_{PP} are the molar mass in g mol^{-1} of acrylamide, acrylic acid and the initiator, respectively.

Table 3. Variation of the volume swelling (S), the volume fraction of the polymer in the swollen gel (υ_S), the Flory–Huggins interaction parameter (χ), the number-average molar mass of the chain between crosslinks (Mc) and the crosslink density (q) with PP content and irradiation dose

Samples	S	$\upsilon_{S\,(cm^3)}$	χ	M_c (g mol^{-1})	M_0 (g mol^{-1})	$qx10^4$
H_{1-1}	96,38	0,0104	0,4278	470.211	136,10	2,89
H_{1-2}	94,03	0,0106	0,4277	450.094	136,10	3,02
H_{1-3}	76,63	0,0131	0,4269	312.353	136,10	4,36
H_{1-4}	70,35	0,0142	0,4266	267.786	136,10	5,08
H_{2-1}	120,35	0,0083	0,4284	695.402	136,37	1,96
H_{2-2}	109,62	0,0091	0,4282	590.203	136,37	2,31
H_{2-3}	74,60	0,0134	0,4268	297.647	136,37	4,58
H_{2-4}	77,48	0,0129	0,4270	318.638	136,37	4,28
H_{3-1}	74,61	0,0134	0,4268	297.743	136,70	4,59
H_{3-2}	70,19	0,0142	0,4266	266.729	136,70	5,13
H_{3-3}	74,40	0,0134	0,4268	296.211	136,70	4,61
H_{3-4}	78,67	0,0127	0,4270	327.434	136,70	4,17

Table 3 shows that the number-average molar mass between the crosslinks of hydrogels increases with PP content and irradiation dose. Since AAm and AA in hydrogels includes many hydrophilic moieties (nonionizable and ionizable), AMD/AA hydrogels can swell significantly. Crosslink density is reverse due to the value of the number-average molar mass between crosslinks.

CONCLUSIONS

This study was carried out to illustrate the synthesis of poly[acrylamide-co-acrylic acid] superabsorbents in the presence of different concentration of initiator under the effect of electron beam irradiation. The characteristics of the superabsorbents are influenced by the chemical composition and the electron beam absorbed dose. In an irradiation cure system, the gel content and the soluble fraction of samples increases with increase of irradiation dose. This is due to the formation of a three-dimensional network structure. The water absorbency of the crosslinked copolymer was measured by swelling in distilled water at room temperature. At high initiator concentrations ($K_2S_2O_8$), more crosslinks could be formed to give rigid chains that reduce the swelling of the gel. The number-average molar mass between crosslinks of hydrogels increases with $K_2S_2O_8$ content and irradiation dose. Crosslink density is reverse due to the value of the number-average molar mass between crosslinks.

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