NRA-1

Characterization and Metal Sorption of Gamma Radiation Copolymerization of Acrylic Acid/ Plasticized Starch /Carboxymethyl Cellulose Mixtures

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Abstract

Copolymers were prepared by gamma irradiation of acrylic acid (AAc)/plasticized starch (PLST)/carboxymethyl cellulose (CMC) mixtures in aqueous solutions. The effect of AAc ratio and gamma irradiation dose on the gel content, swelling (%) and tensile mechanical properties was investigated. The PAAc-*co*-PLST/CMC copolymers were characterized by thermogravimetric analysis (TGA), differential scanning calorimetry (DSC), and surface morphology by scanning electron microscopy (SEM). The thermal stability was further investigated by determining the activation energy by three different methods based on Coats-Redfern, Broido and the Horowitz –Metzger approximation equations. As an application, the removal of copper and nickel ions by the copolymer hydrogel was also studied. The results indicated that the graft copolymer hydrogels have higher affinity for Ni^{+2} than Cu^{+2} ions.

Keywords:
Copolymers; Radiation; Natural Polymers, Acrylic acid; Metal absorption

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1. Introduction

Hydrogels are three dimensional crosslinked polymeric network structures, which have the ability to swell and absorb large amounts of water or biological fluids according to different environmental conditions. The network of hydrogels, particularly those based on natural polymers, can be formed by different methods as chemical initiation or ionizing radiation from one component or two components by copolymerization, inter-polymer complexes and semi-interpenetrating polymerization [1- 4].

Polysaccharides and their derivatives are typical degradable polymers in radiation processing; however, in several studies it was found that polysaccharide derivatives such as carboxymethyl cellulose (CMC), carboxymethyl starch (CMS), and carboxymethyl chitosan undergo crosslinking when irradiated at paste like condition [5-10]. The radiation crosslinking of polysaccharides was proposed to occur via increased mobility of its molecules in water and the formation of CMC radicals from the abstraction of H atoms from macromolecules in the intermediate products of water radiolysis, particularly the OH radicals according to the following equation [11]:

$$H_2O \xrightarrow{\text{Gamma irradiation}} e^-_{aq}, OH^\bullet, H^\bullet, H_2O_2, H_2$$

Cellulose is one of the most important abundant materials in nature. Few studies have been reported in literature on the grafting of vinyl monomers onto cellulose either by ionizing radiation or chemical initiation. In this contest, granular maize starch was grafted by acrylic acid (AAc) in aqueous medium initiated by ceric ion (CAN) [12]. The factors that may affect the grafting such as concentrations of ceric ion (CAN) and AAc, reaction temperature, polymerization time and material-to-liquor ratio were studied. The optimum conditions obtained for the grafting of AAc onto 2 g of granular maize starch were: [AAc] = 0.2775 mol/L; [CAN] = 0.004 mol/L; time = 240 min; temp = 35°C; material-to-liquor ratio = 1:10. Ceric ammonium nitrate as initiator was also used for acrylic acid (AAc) and acrylonitrile (AN) monomers grafting onto cellulose fluff pulp [13]. Antimicrobial activity of the grafted cellulose samples was studied against *Escherichia coli*, *Pseudomonas aeruginosa* and *Bacillus subtilis* and proved that the synthesized biomaterial was effective, very simple and practical to the textile finishing industry. Cellulose-based super absorbent was prepared from radical graft copolymerization of AAc and AM onto flax yarn waste using APS as the initiator in the

presence of an N, N′-methylenebisacrylamide (MBA) as a crosslinking agent [14]. The method used was a free-radical graft copolymerization of AAc and AM.

The synthesis and applications of copolymer hydrogels based on vinyl monomers and CMC have been studied in literature by radiation and chemical initiation. Super absorbent polymer was synthesized by radiation-induced grafting of acrylamide onto carboxymethyl cellulose (CMC) in the presence of MBA as a crosslinking agent [15]. The graft copolymer was loaded with potassium nitrate (KNO$_3$) as an agrochemical model and its potential for controlled release. Superabsorbents were synthesized by graft copolymerization of acrylic acid/acrylamide/2-acrylamido-2-methyl-1-propanesulfonic acid onto sodium carboxymethyl cellulose (CMC) and montmorillonite (MMT) by using potassium persulfate (KPS) as a free radical initiator, in the presence of MBA as a crosslinking agent [16]. The synthesis of carboxymethyl cellulose (CMC)-g-polyacrylamide (PAM) was carried out in an aqueous medium by using a redox system as an initiator [17]. Graft polymerization was employed to produce an adsorbent using acrylic acid and carboxymethyl cellulose for dye removal [18]. Carboxymethyl cellulose-g-poly (acrylic acid)/attapulgite (CMC-g-PAA/APT) hydrogel composites was prepared and used for Pb(II) adsorption from aqueous solution [19]. The synthesis of polyacrylic acid grafted carboxymethyl cellulose (CMC-g-PAA) was developed using microwave radiation alone to initiate the grafting reaction [20]. The application of the grafted product as flocculent for river water clarification, towards augmentation of drinking water supply was investigated.

The present work involves three major objectives: (1) the preparation of copolymer hydrogels by gamma irradiation of acrylic acid monomer (AAc)/plasticized starch (PLST)/ carboxymethyl cellulose (CMC) mixtures in aqueous solutions. (2) The characterization of the physical and chemical properties of AAc-co-(PLST/CMC) copolymer hydrogels by different techniques. (3) Study the adsorption of copper and nickel ion metals by the copolymer hydrogels.

2. Experimental

2.1. Materials

Maize starch used in this study was supplied by the Egyptian Company for Starch and Glucose, Cairo, Egypt. Carboxymethyl cellulose (CMC) was a laboratory-grade chemical and purchased from El-Gomhoria for chemicals Co., Cairo, Egypt. Glycerol a laboratory-grade chemical was used as a plasticizer, and was supplied by El-Gomhoria for chemicals Co., Cairo, Egypt. Acrylic acid monomer (AAc) used in this work was a laboratory-grade chemicals and obtained from Aldrich Company, USA.

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2.2. Gamma radiation grafting of AAc onto PLST /CMC mixtures

Plasticized starch (PLST) was first prepared according to a method described previously [21]. The PLST and CMC polymers were devolved in aqueous solutions and prepared at the ratios of 80/20 and 70/30-wt %. The AAc ratio was added to the PLST/CMC solutions on behave of the PLST ratio. The AAc/PLST/ CMC solutions were poured into quick-fit glass plates and the contents were made free of oxygen by bubbling nitrogen gas at least for 5 min before being exposed to gamma irradiation. The copolymer hydrogel films were removed and thoroughly washed with hot water to get rid of unreacted materials.

Gamma irradiation to the required doses was carried out in air in the Co-60 gamma cell, at installed at the National Center for Radiation Research and Technology, Cairo, Egypt, a dose rate of 2.4 kGy h^{-1}. The exposure time was adjusted to achieve the required absorbed doses.

2.3. Determination of gel content

A sample of the copolymer hydrogel was accurately weighed (W_o), extracted with distilled water using a soxhlet system and dried in a vacuum oven at $80^{o}C$ to a constant weight (W_1). The gel content was calculated according to the following equation:

$$\text{Gel content } (\%) = (W_1/W_o) \times 100$$

2.4. Swelling characters

The equilibrium swelling study was conducted on the copolymer hydrogels as a function of AAc ratio and irradiation dose. A dry weight of insoluble copolymer (W_d) was immersed in water at pH of 7 up to 24 h at $25^{o}C$, the sample was removed and blotted on filter paper to remove excess water and weighed (W_s). The percentage swelling was calculated according to the following equation:

$$\text{Swelling } (\%) = [(W_s-W_d)/W_d] \times 100$$

2.5. Scanning electron microscopy (SEM)

The morphology of the fracture surfaces of the copolymer hydrogels was examined by scanning electron microscopy (SEM). The SEM micrographs were taken with a JSM-5400 electron microscope made by Joel, Japan. A sputter coater was used to pre-coat conductive gold onto the fracture surfaces before observing the micrographs at 30 kV.

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2.6. Tensile mechanical testing

Mechanical tests including tensile strength and elongation at break point were preformed at room temperature using Instron machine (model 1195) employing a crosshead speed of 5 mm/min. For this test, the films were cut with a die in a dog-bone shape. The recorded value for each mechanical parameter is the average of five measurements.

2.7. Thermal analysis

Thermogravimetric analysis (TGA) was carried out using a TG-50 instrument from Shimadzu (Japan) with a heating rate of 10°C/min. The differential scanning calorimetry (DSC) measurements were performed using a Shimadzu DSC-50 Calorimeter equipped with data station. A heating rate of 10°C/min was utilized and the scans were carried out under a flowing nitrogen atmosphere at a rate of 20 ml/min.

2.8. Determination of metal uptake

The metal uptake was determined by immersing constant weight (W) of the copolymer hydrogel in the different metal solutions of constant concentration (mg/L) until equilibrium. The remaining metal concentration in solution was determined by atomic absorption instrument (Unicam model Solaar 929). The metal uptake was determined as follows:

$$\text{Metal uptake (mg/g)} = (C_o - C_1)/W$$

Where C_o is the initial concentration of metal ions, C_1 is the concentration of the metal ions adsorbed on the hydrogel and W is the mass of hydrogel.

2.10. FT-IR spectroscopy

The IR spectra were recorded by using ATI Mattson FT-IR spectroscopy, Genesis series, Unicam, England at a resolution of 4 cm^{-1}. The spectra of the investigated samples were measured directly after irradiation.

3. Results and discussion

3.1. Gamma radiation synthesis of PAAc-*co*-(PLST /CMC) copolymer hydrogels

The formation of the copolymer hydrogels may be proposed to occur through the following procedure:
   a) Acrylic acid (AAc) monomer is known to undergo polymerization and subsequently crosslinking by gamma radiation to form crosslinked network hydrogels as reported

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early **[11]**. When an aqueous solution of AAc/PLST/CMC mixtures is exposed to gamma irradiation, free radicals are formed on the chains of both species. Also, the radiolysis products of water especially **HO˙ and H˙** free radicals, are very effective in generally free radicals on both PLST and CMC. The transfer of radicals from water to polymers increases the concentration of PAAc radicals and thus increases the rate of copolymerization.

b) As shown in the introduction section, CMC will undergo crosslinking and form network structure. Thus, it is possible that networks could be formed between crosslinked AAc and CMC and a graft copolymer could be formed, in which AAc is grafted onto either CMC chains or crosslinked networks.

c) In summary, an interpenetrating network structure (IPN) could be formed, in which PLST is physically included in the networks of crosslinked PAAc and CMC as proposed schematically in **Fig.1**. Initiation takes place on AAc and CMC chains, grows, and finally gets copolymers and crosslinked networks **[22, 23]**. The formation of a graft copolymer of AAc onto PLST/CMC is also possible.

3.1.1. Gel content and swelling characters

Fig.2 shows the effect of AAc ratio on the gel content (%) and swelling (%) of PLST/CMC (80/20%) copolymer hydrogel, prepared at different doses of gamma irradiation. It can be seen that the gel content increases with increasing the AAc ratio up to 10% and then tends to level off at higher ratios. The gel content was found to increase slightly by increasing the irradiation dose. However, at higher doses, the gel content tends to increase slightly due to the degradation of PLST polymer.

The swelling behavior of polymeric systems has a great importance when it is applied in the metal sorption as its hydration degree influences on the surface properties and mobility, on its mechanical properties and on the type of solute transport mechanism through the hydrogels**.** As shown in **Fig.2**, two points may be addressed:

(1) The swelling increases with increasing AAc ratio, regardless of irradiation dose.

(2) In general, the swelling (%) was found to decrease with increasing irradiation dose in accordance with the gel content, in which the copolymerization of highly hydrophilic polymer onto highly hydrophilic polymers would enhance the diffusion of high quantities of water into the copolymer structure and hence increasing swelling. The possible formation of network structure due to the crosslinking of AAc and CMC will reduce the diffusion of water particularly at higher irradiation doses.

3.1.2. Tensile mechanical properties

Mechanical properties such as tensile strength and elongation of hydrogels may constitute an important property when the hydrogels has to be applied as metal adsorbents. **Fig.3**

shows the effect of AAc ratio on the tensile strength and elongation at break of PLST/CMC (80/20%) copolymer hydrogels, prepared at different doses of gamma irradiation. Based on these figures, two points can be summarized:

a) The tensile strength of the copolymer hydrogels increases with increasing AAc ratio and irradiation dose. The formation of copolymerization of AAc with branched structure or the possible occurrence of crosslinking, associated with increasing irradiation dose, will cause the graft copolymer to resist the tension and thus increases the tensile strength.

b) Elongation at break was found to decrease with increasing irradiation dose and AAc ratio. Once again, this behavior can be attributed to the compact structure of the copolymer hydrogels resulting from the increased branching density. Therefore, the tensile strength and the elongation of the graft copolymer hydrogels can be controlled by the composition as well as the dose.

3.1.3. Scanning electron microscopy

Fig.4 shows the SEM micrographs of the fracture surfaces of PAAc-g-(PLST/CMC) (80/20%) copolymer hydrogels containing different gel contents. In compatible copolymers, the mechanical properties will depend on the phase dispersion as well as on phase size. As can be seen from **Fig.4A**, the fracture surface of unirradiated PLST/CMC blend is smooth, continuous phases and there is no indication of phase separation. However, the SEM micrographs of PAAc-g-(PLST/CMC) copolymer hydrogel showed a different surface morphology, in which the surface is rough and characterized with the presence of wrinkles and cavities. This texture was found to increase with increasing the gel content. In this case, this texture is due to the grafting and the possible crosslinking of AAc and CMC components.

3.1.4. Thermogravimetric analysis (TGA)

The thermal stability of any polymeric materials is largely determined by the strength of the covalent bonds between the atoms forming the polymer molecules. Also, intermolecular hydrogen bonds or covalent bonds between the polymer chains are expected to increase the thermal stability. The reported bond dissociation energy values for C-H, C-C, C-O, O-H, C=O and C=C was 414, 347, 351, 464, 741 and 611 kJ/mol, respectively **[24]**. According to these values, the average dissociation energy (ADE) for PAAc $\{- [CH-CH_2 (COOH)]_n\}$, as an example as follows:

$$ADE = 3 (C\text{-}H) + 2 (C\text{-}C) + 1 (C=O) + 1(C\text{-}O) + 1 (O\text{-}H) = 3X314 + 2X347+741+464+351= 3192/8=399 \text{ kJ/ mol.}$$

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For PLST and CMC, the ADE was calculated to be 385.9 and 578 kJ/ mol, respectively. According to these values, it may expect that copolymer hydrogels based on PAAc and CMC will possess higher thermal stability than PLST polymer.

Thermogravimetric analysis (TGA) was used to investigate experimentally the thermal stability of unirradiated and irradiated polymer blends. **Fig.5 and 6** show the TGA thermograms and the corresponding rates of the thermal decomposition reaction of different ratios of PLST/CMC blends and AAc/PLST/CMC copolymer hydrogels of 55% gel content, prepared by gamma irradiation. The weight loss (%) at different temperatures of unirradiated PLST/CMC blends of different ratios and their corresponding graft copolymers with acrylic acid (graft yield of 55%) is shown in **Table 1**. As shown, the TGA thermograms indicated that the PAAc-*co*-(PLST/CMC) copolymer hydrogels are thermally more stabile than the unirradiated PLST/CMC blends. This is due to the formation of copolymerization and subsequently crosslinking by gamma irradiation. It can be also seen that the rate of thermal decomposition reaction (dw/dt) for either unirradiated blends or their copolymer hydrogels goes through one maximum over the entire range of temperature. However, the temperature of the maximum value of reaction rate (T_{max}) differs from one material to another. In this regard, the T_{max} for PLST/CMC (80/20%) and PLST/CMC (70/30%) blends was found to be 328.5 and 353.9°C, respectively, whereas for those of PAAc-*co*-(PLST/CMC) (80/20%) and PAAc-*co*-(PLST/CMC) (70/30%) copolymer hydrogels with 55% gel content were found to be 347.4 and 364.0°C, respectively. These values indicate that the increase of CMC ratio in the blends resulted in an increase in the thermal stability, whereas a further increase in the T_{max} was observed after copolymerization with acrylic acid.

The thermal stability of the graft copolymers was further confirmed by determining the activation energy of the thermal decomposition. Three different non-isothermal methods were used including the methods of Coats-Redfern **[25]**, Broido **[26]** and the Horowitz – Metzger **[27]**.

For a first-order reaction process, Coats-Redfern proposed an approximation as shown in equ.1:

$$\ln [-\ln (1- \alpha)/T^2] = -E_a/RT + \ln AR/\beta E_a \qquad (1)$$

Where α is the fraction of sample decomposed at temperature T, A is constant, β is heating rate, R is universal gas constant and E_a is the activation energy. Therefore, plotting $\ln [-\ln (1- \alpha)/T^2]$ vis.1/T should give a straight line whose slope is directly

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proportional to the activation energy (E_a/R). Horowitz-Metzger proposed an equation for the calculation of activation energy (E_a) of polymeric substances as shown in equ. 2:

$$\ln[-\ln(1-\alpha)] = E_a\,\theta/RT_s^2 \qquad (2)$$

Where α is the fraction of sample decomposed at temperature T, θ is the difference between the peak temperature and the temperature at particular weight loss ($\theta = T - T_s$); T_s is the peak temperature; and T is the temperature at particular weight loss. A plot of $\ln[-\ln(1-\alpha)]$ vs. θ gives an approximation to a straight line. From the slope, the activation energy (E_a) can be calculated.

Broido developed an equation used for the calculation of activation energy (E_a) as shown in equ.3:

$$\ln\ln(1/Y) = (-E_a/R)\,1/T + \text{constant} \qquad (3)$$

Where Y is the fraction of the number of initial molecules not yet decomposed:

$$Y = (W_t - W_\infty)/(W_o - W_\infty)$$

Where W_t the weight at any time t; W_∞ is the weight at infinite time (=zero) and W_o is the initial weight. A plot of $\ln\ln(1/Y)$ vs.$1/T$ gives an approximation to a straight line. The slope is related to the activation energy.

Fig.7 shows plots of $\ln[-\ln(1-\alpha)]$ against θ ($\theta = T-T_s$) for unirradiated PLST/CMC blends and the same blends after copolymerization with PAAc at a constant gel content of 55% by gamma irradiation according to Horowitz-Metzger equation (as an example). However, the activation energy calculated and the corresponding regression values (r^2) based on the three different methods are shown in **Table 2**. Based on the plots and the data on **Table 2**, two points may be concluded:

(1) In general, the activation energy of PVA/MC blends, either before or after gamma radiation copolymerization, calculated by the three methods is comparable indicating the good fitting to the approximation to a straight line by these methods. The corresponding regression values (r^2) based on the three methods indicate clearly the fitting to the straight lines as shown in **Table 2**.

(2) It can be seen that the PAAc-co-(PLST/CMC) copolymer hydrogels displayed higher energy of activation when compared to that of unirradiated blends. These findings were observed by the three methods used. However, the thermal stability was found to increase by increasing the CMC ratio.

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3.1.5. Differential Scanning Calorimetry (DSC)

Differential scanning calorimetry (DSC) technique is one of the convenient methods for investigating the compatibility of polymer blends. It was used to investigate the effect of blending and gamma- radiation copolymerization with AAc. **Fig.8** shows the DSC thermograms of PLST/CMC of different compositions before and after they had been gamma-radiation copolymerized with PAAc at a constant gel content of ~ 55%. Based on the DSC scans, two points can be observed:

a) The onset T_c of ungrafted PLST/CMC (80/20%) unirradiated blend can be detected at 234.8^{o}C, whereas the onset T_c of unirradiated PLST/CMC (70/30%) blend can be detected at 233.08^{o}C.

b) For the PAAc-*co*-(PLST/CMC) copolymer hydrogel at the ratio 80/20%, the onset T_c was at 240.4-241.5^{o}C, whereas the onset T_c for the copolymer hydrogel at 70/30% was found at 234.9^{o}C.

3.2. Sorption of Heavy metals

3.2.1. Metal uptake

Films of PLST/CMC blend and their copolymer hydrogels with constant gel content of ~45% were washed wth NaOH solution and then impregnated in 25 ml of solution containing different metal ions (Cu and Ni) for 24 hour. **Fig.9** shows the equilibrium uptake of copper and nickel ions by PLST/CMC blends before and after gamma-radiation copolymerization with constant gel content of ~ 45%. It can be seen that the PAAc-co-(PLST/CMC) copolymer displayed higher metal uptake than the unirradiated blends. This is due to the presence of carboxylic groups capable to react with the metal ions. On the other hand, further metal uptake can be adsorbed by the copolymer hydrogels due to the presence of additional carboxylic groups from PAAc.

3.2.2. FT-IR analysis

FTIR spectroscopy was used to verity the change in the chemical structures of AAc-co-(PLST/CMC) copolymer hydrogels loaded with Cu ions. **Fig.10** shows the FT-IR spectra of PLST/CMC blends and PAAc-*co*-(PLST/CMC) copolymer hydrogels containing a constant gel content of ~ 45%, before and after loading with copper ions. The FT-IR spectra of all the copolymer hydrogels either before or after loading with copper ions showed characteristic absorption peaks at 3300-3900 cm^{-1} due to of O-H groups, at 2924 cm^{-1} due to the C-H stretching, at 1649 cm^{-1} and 1432 cm^{-1}correspond to OH and CH bending **[28]**. On the other hand, the copolymer hydrogels loaded with Cu ions showed a strong absorption band at 1749 cm^{-1} attributed to the stretching of the ester carbonyl C=O, which was shifted duo to coordination of -COO with Cu ion. Also, a small narrowing in the bands at 3600–3000 cm^{-1} can be seen, which is due to the coordination of the

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hydroxyl groups with the Cu^{2+}. The shoulder at 1540 cm^{-1} corresponds to –OH bending was shifted and a new band at 1108 cm^{-1} was seen corresponds to the complexes with Cu ions. Based on the above analysis, several points may be addressed:

a) The shift in the absorption band due to -OH stretching in the case of hydrogels loaded with Cu ions is due to the interaction between copper ions and COOH groups to form complexes [29]. The shift in the 1550 and 1540 cm^{-1} band frequencies are due to the involvement of these groups in the coordination with Cu^{2+}.

b) The narrowing in the bands at 3600–3000 cm^{-1} is a clear indication about the involvement of–OH groups in the coordination with the metal ion. Also, this coordination prevents the hydrogen bonding between hydroxyl groups, i.e., prevents the broadening at 3600–3000 cm^{-1}.

4. Conclusions

In this work, acrylic acid monomer was copolymerized with natural blends composed of plasticized starch (PLST) and carboxymethyl cellulose (CMC) by gamma irradiation. It was found that the ratio of AAc and CMC determines the physical and chemical properties of graft copolymer. Depending on the presence of plenty of carboxylic groups on the macrostructure of the copolymer hydrogels, it was used for the removal of Cu^{+2} and Ni^{+2} ions. In addition to formation of copolymers was also possible, in which both acrylic acid and CMC will undergo induced crosslinking and thus interpenetrating networks (IPNs) could be formed. This type of reactions will increase the capability of the copolymer hydrogels for much metal removal.

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Table 1.Weight loss at different temperatures of unirradiated PLST/CMC blends of different ratios and their corresponding graft copolymers with acrylic acid (graft yield of 55%)

PLST/CMC copolymers	Weight loss (%)					T_{max} (^{o}C)
	100°C	200°C	300°C	400°C	500°C	
80/20% (unirradiated)	12.00	16.97	50.23	72.60	92.69	328.5
70/30% (unirradiated)	7.31	8.68	35.16	59.09	84.11	353.8
80/20% graft copolymer	4.25	9.74	55.64	73.83	93.14	347.4
70/30% graft copolymer	3.98	9.62	51.95	86.43	99.17	364.0

Table 2: Energy of activation of PLST/CMC (%) blends at different ratios and their corresponding copolymers with a constant gel content of 55% determined according to Coats-Redfern, Horowitz-Metzger and Broido equations with maximum R^2 value.

PLST/CMC copolymers (%)	Activation energy (kCal/mol)					
	Coats-Redfern		Horowitz-Metzger		Broido	
	E_a	r^2	E_a	r^2	E_a	r^2
80/20% (unirradiated)	6.7100	0.967443	٩.٣٠٦٢	0.971104	6.7100	0.967444
70/30% (unirradiated)	7.8918	0.961415	١٠.٩٣٥٤	0.953268	7.8918	0.961415
80/20% copolymer	10.3756	0.980817	١٢.٨٢٠٥	0.963896	9.1063	0.954541
70/30% copolymer	11.4040	0.975789	١٤.٦٥٣٨	0.966166	10.6678	0.981621
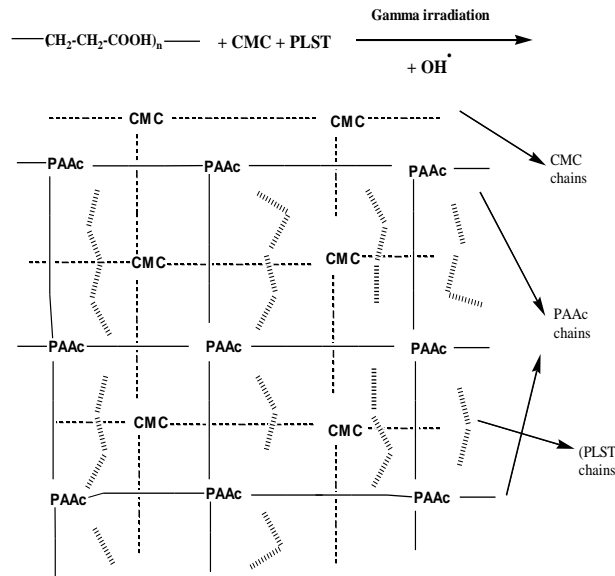
Fig.1.Schematic diagram of the proposed interpenetrating (IPN) networks of AAc-*co*-(PLST/ CMC) copolymer hydrogels, formed by gamma radiation.
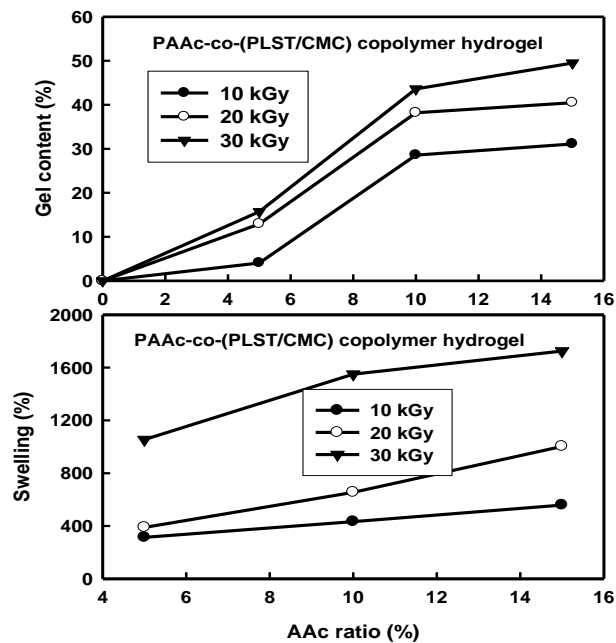

Fig.2. Effect of AAc ratio on the gel content and swelling (%) of PLST/CMC (80/20%) copolymer hydrogels, prepared at different doses of gamma irradiation.
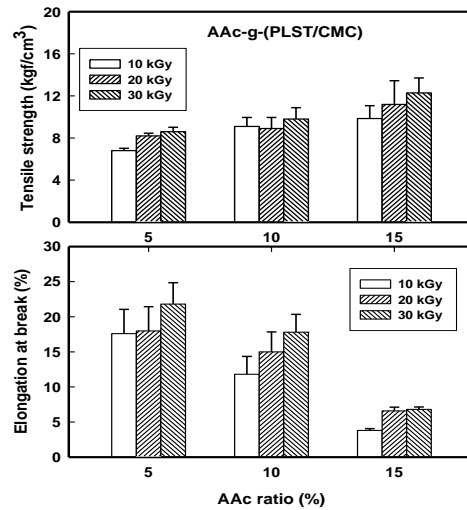
Fig.3. Effect of AAc ratio on the tensile strength and elongation at break of PLST/ CA/CMC (80/20%) copolymer hydrogels, prepared at different doses of gamma irradiation.
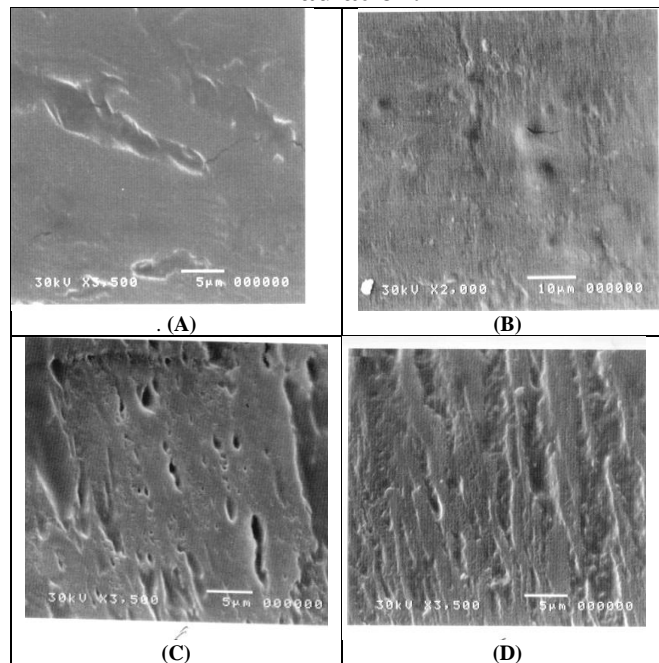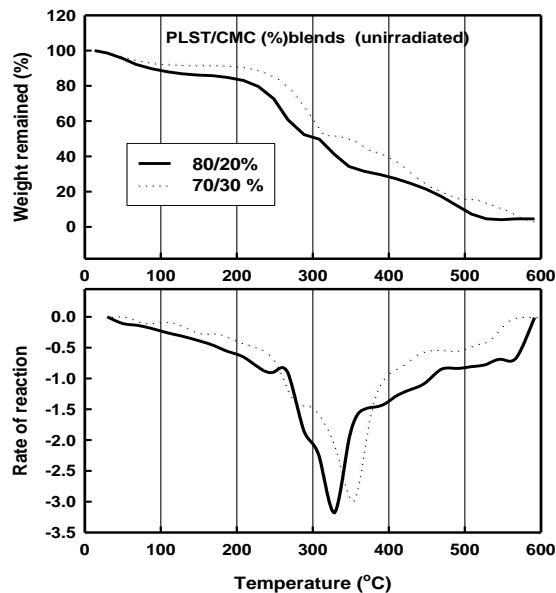

Fig.4. SEM micrographs of the fracture surfaces of PLST/CMC (80/20%) blend with deferent gel content: (A) unirradiated, (B) gel content of 28% (D) gel content of 38%, (E) gel content of 55%.

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Fig.5. TGA thermograms and the corresponding rates of the thermal decomposition reaction of unirradiated different ratios of PLST/CMC blend.
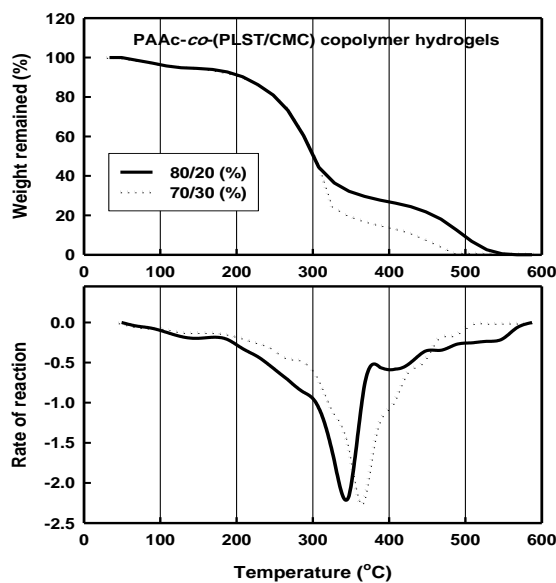
Fig.6. TGA thermograms and the corresponding rates of the thermal decomposition reaction of AAc/PLST/CMC copolymer hydrogels of 44% gel content, prepared by gamma irradiation at a dose of 30 kGy.

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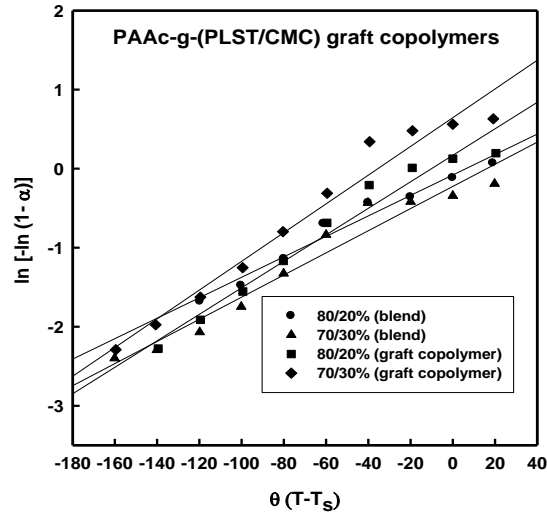**Fig.7. Plots of ln [-ln (1- α)] against θ (θ = T – T$_s$) for ungrafted PLST/CMC blends and the same blends grafted with PAAc at a constant of graft yield of 44% by gamma irradiation according to Horowitz-Metzger equation.**
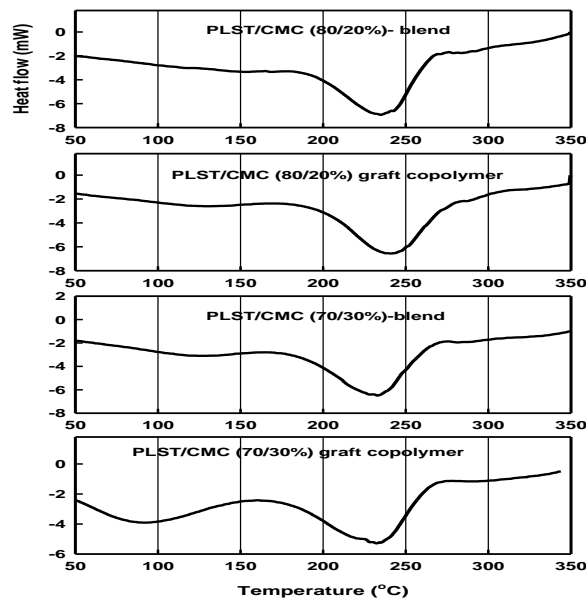

Fig.8. DSC thermograms of PLST/CMC of different compositions before and after they had been gamma-radiation copolymerized with PAAc at a constant gel content of ~ 55%.

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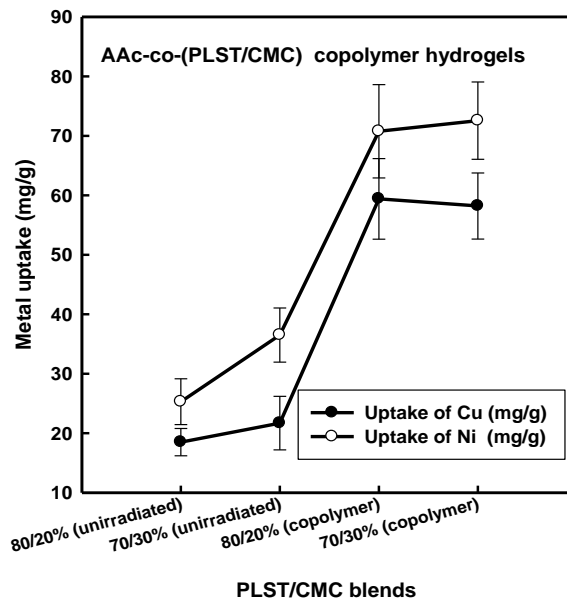on
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Fig.9. Uptake of copper and nickel ions by PLST/CMC blends before and after gamma-radiation copolymerization with a constant gel content of ~ 45%.
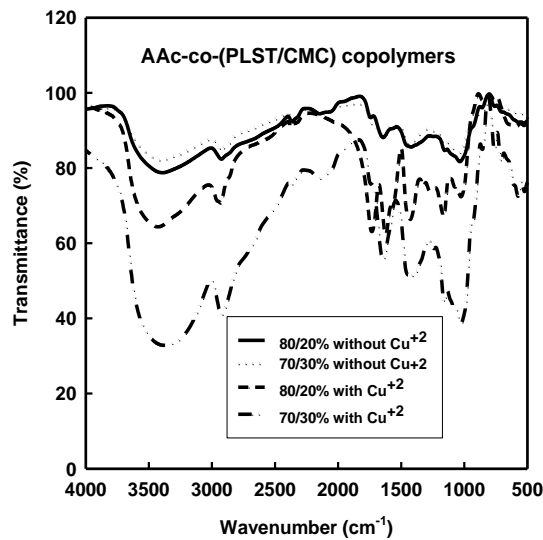

Fig.10. FT-IR spectra of PLST/CMC blends and PAAc-co-(PLST/CMC) copolymer hydrogels containing a constant gel content of ~ 45%, before and after loading with copper ions.