Gamma Radiation Polymerization Induced Grafting For Application In Drug Release Systems.

Nabila Ahmed Maziad[1], Sabrnal El-Hamouly[2], Ebrhem zied[3] and Nada Rabie Nasef[4]

[1]Dpartment of Polymer Chemistry National Center for Radiation Research and Technology, Atomic Energy Authority, Egypt.
[2]Chemistry Department, Faculty Of Science, Manoufia University, Egypt.
[3]Organic Chemistry Department, Faculty of Science, Manoufia University, Egypt.
[4] Chemistry Department, Faculty Of Science, Manoufia University, Egypt.
Nabila_Maziad@yahoo.com

Abstract: Radiation grafting of monomers onto low density polyethylene is a useful tool for tailoring new polymers for special purpose. This study aims to prepare low density polyethylene films grafted with acrylic and methacrylic acid. Different factors affecting the reaction conditions on the grafting yield, such as the irradiation dose and monomer concentration, type of inhibitors, and inhibitor concentrations has been studied. The prepared grafted membranes were characterized to determine the structural changes with Fourier transform infrared (FTIR) spectroscopy. The morphological structure using X–ray diffraction analysis and scanning electron microscopy (SEM) have been studied. The swelling properties of the prepared copolymers have been studied at different time and different pH. It was found that the swelling percent increases as the time increase and found that (LDPE-g-PMAAc) increases more than (LDPE-g- PAAc). From Study of different pH it was found that the high pH for (LDPE-g- PAAc) and (LDPE-g- PMAAc) at the same pH_7. Study of drug loading and drug controlled release versus the degree of grafting, drug concentration and different time intervals. It is found that as the degree of graft increases the loading percent increase. Also, the controlled release of drug increased as time increases and the maximum release occurred after 24 h.

[Nabila Ahmed Maziad, Sabrnal El-Hamouly, Ebrhem zied and Nada Rabie Nasef. **Gamma Radiation Polymerization Induced Grafting For Application In Drug Release Systems.** *J Am Sci* 2015;11(4):77-89]. (ISSN: 1545-1003). http://www.jofamericanscience.org. 9

Key words: Gamma radiation, Grafting, LDPE film, Drug Release.

1- Introduction

The radiation-induced graft copolymerization as a method of modification of polymeric materials has been extensively used over recent years [(1)].

Graft polymerization can be initiated by using gamma rays is one of the most promising methods, because of ease of creation of active sites for initiating grafting through the matrix of a polymeric substrate and moderate reaction conditions[(2,3)]. It allows introducing active functional groups to the surface of plastic films after modification [(4)]. Radiation-induced graft polymerization being both economical and environmentally clean technique [(2,3)]. The radiation-induced grafting method is the most effective for the introduction of the graft polymer chains, because the molecular chains can propagate through radical species that are generated inside and outside of the film by irradiation [(5,6)]. By controlling the experimental conditions (monomer concentration, gamma radiation dose-rate and irradiation environment), one can tailor the final properties of the samples in order to produce new materials for specific applications [(5,7,8,9)]. Radiation grafting Under appropriate experimental conditions, modifications of polymer properties can be accomplished not only at the surface but also throughout the polymer[(10)]. Grafting processes may be carried out under simultaneous treatment conditions, with all components being present during the creation of reactive sites. Alternatively, grafting can be performed via pre-activation process. Reactive sites are generated in the absence of the modifying species, but subsequently exposed to modifying species under some predetermined and controlled condition [(11)]. Other methods have been developed such as atom transfer radical polymerization [(12,13)] or "living" radical polymerization [(14,15)]. These methods allow in controlling the length of grafts since they act more efficiently on the kinetics of the chain growth [(16)]. Radiation-induced grafting is a powerful tool capable of controlling the introduction of various functional groups to the polymeric materials, keeping the original properties and especially the mechanical strength of the base material, and thus, allowing the synthesis of more stable polymeric adsorbents[(17)]. Low density polyethylene (LDPE) is most commonly used as plastic and has been extensively used as a backbone for irradiation grafting with different monomers [(5,18)]. In spite of the highly complex structure of polyethylene, which makes it particularly difficult to interpret the experimental results. Diffusion of the monomer being grafted into the host polymer is an

important part of the grafting process. However, due to the crystallinety of low density polyethylene (LDPE), the diffusion of monomer into it is limited because the swelling of LDPE in most monomers at room temperature is generally[19,20]. The direct grafting method of acrylic acid onto LDPE films results in a cross-linked gel of PE and the formation of poly acrylic acid homo polymer. The separation of the entrapped film from the hydrogel is difficult. Many workers have added Mohr's salt to decrease homo polymerization[21]. In the grafting of acrylic acid and methacrylic acid onto LDPE, the trapped radicals formed by irradiation are able to induce graft polymerization[22-25]. The disorder promoted in the molecular structure of PE due the grafting process, when gamma radiation is used as the energetic source coefficients of other species deep inside the polymeric matrix, increasing the material hydrophilicity. Aiming at the production of new grafted co polymeric LDPE films, suitable to be used for bio applications, we have prepared and characterized (LDPE-g-AAc) and (LDPE -g- MAAc) copolymers [26].

This work aims to prepare LDPE film grafted (AAc, MAAc) monomers and study their application in drug releasing and study of their antibacterial activity for gram positive and gram negative.

2. Experimental

2.1. Material

Pure Acrylic Acid (AAc) from (Aldrich)of purity 99% was used as received (C3H6O2), Methacrylic Acid (MAAc) 98.5% (C4H6 O2), Low density Poly Ethylene films (LDPE) of thickness (70 micron) were grafted with AAc and methacrylic from EL-Nasr Co. for medical Supplies, Cairo, Egypt. Buffer Solutions of pH range (2 to 12). Other chemicals were used as received without further purification.

2.2. Graft Copolymerization onto (LDPE).

Strips of Low density polyethylene (LDPE) films were washed with acetone, dried at 60^0 C in vacuum oven, weighed and then immersed in corresponding monomer solution in glass tubes. Homo polymerization inhibitors such as cupper sulphate, ammonium ferrous sulphate, and ferric chloride were introduced in employed monomer solutions. On the direct radiation grafting method was carried out under nitrogen gas. In this case, the glass tube containing the monomer solution and films was exposure by bubbling nitrogen for (4-7) min, and then sealed and subjected to ^{60}Co gamma - rays at different radiation (kGy/h). the grafted films were removed and washed thoroughly with acetone to extract dose the residual monomer and the homo polymer which may be formed in the film.for instance, poly (acrylic acid) and (methacrylic acid) were removed by washing grafted films thoroughly with hot distilled water and soaked overnight in water to extract the residual monomer and the homo polymer which may be occluded in the film. The obtained grafted films were dried in a vacuum oven at ($50\ ^0$C - $60\ ^0$C) for 24 h and weighted. The degree of grafting was determined by the percentage increase in the weight as follows:-

Degree of grafting (%) = [(W g – W 0)/W0] × 100 [1]

Where W0 and Wg represent the weights of initial and grafted films, respectively.

2.3. Preparation of Buffer Solutions of Different pH.

(Citric acid/ trisodium citrate) and (Sodium dihydrogen phosphate/ disodium hydrogen phosphate) were used to prepare buffer solutions of pH values ranged from 3-5 and 6-7, respectively[27,28].

2.4. Swelling Measurements.

Swelling experiments were performed by placing the prepared films discs in buffer solutions of varying pH of (2-12) at 37°C and measuring Sample weight given as a function of time. The discs were withdrawn from the buffer solutions and weighed after removal of excess surface water by gentle blotting with a paper tissue. Percent swelling is expressed as the percent weight ratio of water held in film to dry film at any constant time. The swelling ratio was calculated as shown in equation[2]:

% swelling = [(weight of swelled film–weight of dry film)/weight of dry film]x 100 [2]

2.5. Drug Loading Efficiency and Drug Release.

Ciprofloxacin (CPFX) was used a model drug. The disc samples (LDPE-g- PAAc) and (LDPE-g-PMAAc) (1 g ± 0.0001), were accurately weighted and immersed in solution of ciprofloxacin (CPFX, 0.54 g dissolved in 50 mL of buffer solution) at 37°C for 24 h. The loading amount of drug in the films were calculated from the decrease in the concentration of the CPFX solution which was determined using UV spectrophotometer at 400 nm. The loading efficiency of the (LDPE-g- PAAc) and (LDPE -g- PMAAc) were calculated as the ratio of the final to the initial CPFX concentration.In drug release of (LDPE-g- PAAc) and (LDPE-g- PMAAc) were dipped in (CPFX) putting in the buffer solution and then At specific time Intervals, 4 mL of solution was withdrawn and after suitable dilution the concentration of drug released was measured by UV spectrophotometer at 400 nm. The drug release percent was calculated twice using the following equation [3].

Released drug (%) = Rt / L × 100 [3]

where L and Rt represent the initial amount of drug loaded and the final amount of drug released at time (min).

3. Measurements:

3.1. Gamma Radiation Source.

The samples were carried out using (^{60}Co) by the "simultaneous irradiation grafting" methods in an aqueous solution and different doses the irradiation facility was constructed by the national for radiation Research and Technology (NCRRT), Atomic Energy Authority of Egypt.

3.2. Ultraviolet (UV) Measurements.

Determination of the loading and release amount of drug ciprofloxacin were carried out using JASCO V560spectrophotometer in the range from 200-900nm.the concentration of ciprofloxacin drug were measured at 400nm.

3.3. Scanning Electron Microscopy (SEM).

The dry sample, spread on a double sided conducting adhesive tape, pasted on a metallic stub, was coated 100 micron with gold in a sputter coating unit 2 min and absorbed in electron microscope at 20 kV.

3.4. Fourier Transform Infrared (FTIR) Spectroscopic Analysis.

Polymerization [29,30]of cross-linked samples was monitored by the potassium bromide pellet method. All the spectra were recorded between 4000 and 400 cm-1 using a FTIR spectrometer (FTIR 8400 S, Shimadzu).

3.5.X-Ray Diffraction (XRD).

XRD spectra of drug-loaded and unloaded onto LDPE film were recorded using Bruker D8 Discover apparatus (Germany). Eva software was used for the data processing (Evaluation Package Bruker, Germany). Patterns were obtained at a scan speed of 4º/minute with 2θ between 8° and 20°.

3.6. Microbial Strains.

The bacterial and fungal strains used in this study were obtained from the Microbiology Laboratory, Department of Microbiology, National Center for Radiation Research and Technology, NCRRT, Atomic Energy Authority, Cairo, Egypt. Tested yeast isolates are *Candida albicans, Saccharomyces cerevisiae and rhodotorula glutinis.* Gram-positive bacteria *Staphylococcus aureus an*d Gram-negative bacteria are *Pseudomonas aeruginosa, Salmonella tophi* (non lactose fermenter) and (Lactose fermenter) *Escherichia coli and Klebsiella pneumonia*. All the microorganisms used are checked for purity and maintained at 4°C in slants of nutrient agar and malt extract agar for bacteria and yeast, respectively [51].

3.7. Preparation of inocula.

A loopful of each microbial isolates is transferred from new slant into 25 ml broth medium in 250-ml Erlenmeyer flasks and cultivated on a rotary shaker at 100 rpm for 18 hrs at 37 °C for bacteria, and for 48 hrs for yeasts. Inocula were prepared by transferring into (5 ml) 0.9 % sterile saline solution to obtain the required working suspensions, 10^8 cfu/ml for bacteria and 10^7cfu/ml for yeasts. The bacterial suspension was adjusted with sterile saline to an optical OD (optical density) of 0.2-0.3.

3.8. Antibacterial activity.

Disk diffusion test. *Staphylococcus aureus, Pseudomonas aeruginosa, Klebsiella pneumonia, Salmonella typhi and Escherichia coli,* were used in order to investigate the antibacterial activity of the synthesized grafted film as a polymeric compounds. The bacterial suspension was adjusted with sterile saline to an optical OD (optical density) of 0.2-0.3. The inocula were daily prepared and stored at 4°C until use. Dilutions of the inocula were cultured on solid medium to verify the absence of contamination and to check the validity of the inoculums.

3.9. Preparation of plates:

Mueller Hinton agar medium composed of 1gm laboratory lemco, 2g yeast, 5g peptone, 5g sodium chloride, 20g agar-agar and Distal water 1 liter, Oxoid, were cooked and sterilized at 1 Bar for 20 min. in addition to Muller Hinton broth (lack agar-agar) those are used for bacterial growth. Malt agar medium composed of 30 g Malt extract, 5gm Mycological peptone, 20gm agar-agar and Distal water 1 liter, Oxoid, were cooked and sterilized at 1 Bar for 20 min. in addition to Malt broth (lack agar-agar.).Those are used for yeast growth.

3.10. Antibacterial activity assay of polymeric grafted film:

In vitro antibacterial activity of the synthesized polymeric grafted compounds was determined by the agar disc diffusion method. 18 ml of sterilized Mueller Hinton agar medium was taken in each Petri dish and then spread with a suspension of the tested micro-organism (average concentration is 10^8 cells/ml). 150 µg of each polymer grafted film was placed on the seeded agar plates and then incubated at 37°C for 24 hrs. The antibacterial activity of the test agent was determined by measuring the mean diameter of zone of inhibitions in millimeter.

4. Results and Dissection:

4.1. Effect of Monomer Concentration (AAc and MAAc).

Figure (1) shows the effect of the monomer concentration on the degree of grafting of LDPE film. As can be seen,the grafting degree increase as the monomer concentration increase this behavior can be attributed to diffusion mechanisms as well as a high amount of the monomer (AAc and MAAc) molecules initially available for reaction medium[31,32] there is a tendency of grafting degree to be leveled off and reach saturation state [1,33]. However this might enhance not only the copolymerization reaction but also the homo polymerization reaction. This is pointed out by the percent grafting efficiency [31,32]. Moreover, the degree of grafting increases more as methacrylic acid

concentration increase. As shown at MAAc 30 wt% the film produced is reasonable and flexible film. This may be attributed for the increases of active sites produced after diffusion and increase the grafting. in case of AAc It is clear that the degree of grafting increases by increasing AAc acid to reach a maximum at 30 wt % AAc. Thereafter, any increase in monomer concentration leads to decrease in the grafting degree. Increases the monomer concentration leads to increase the availability of the monomer to reach to the reaction sites on the polymer up to 30wt %. The excess of monomer concentration causes suppression of the monomer diffusion by increasing the viscosity of the grafting medium under the homo polymerization effect which may restrict the grafting percent [34,35].

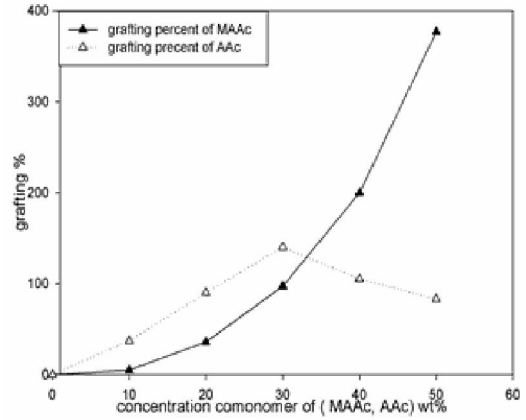


Figure (1): Effect of aqueous acrylic acid and methacrylic acid on the degree of grafting onto LDPE films at 20 kGy.

Effect of Type Inhibitor:

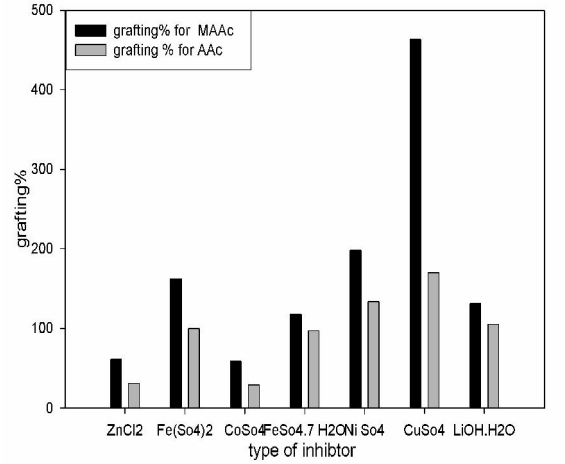


Figure (2): Effect of different type of inhibitors onto grafting using concentration of (AAc and MAAc acid) 30wt% at 20 kGy.

According to the results on figure (1) the suitable concentration of MAAc monomer 30wt%. Studied figure (2) the effect of type inhibitor for the grafting 30wt% MAAc onto LDPE film. It can be seen that the grafting percent increase trough using different inhibitors moreover, it increases more in presence of CuSo4 as inhibitor. the degree of grafting in case of $CuSo_4$ inhibitor reached to 463%.so it is used to enhance and improve the grafting process since the cu ions been attributed to the higher electron affinity of Cu[36,37,38]. Although other metal ion salts causes an increase in, the grafted chain during the irradiation but by less amount and produces a lot of homo polymer which may be restrict the grafting process through the homo polymerization and decreasing the grafting[37,38,40].

The Effect of Different Concentration of Inhibitor

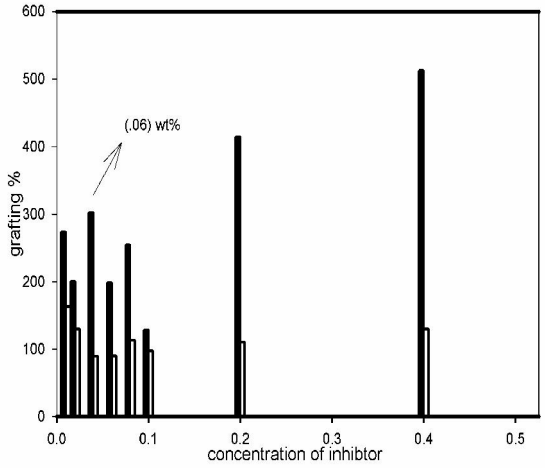


Figure (3): Effect the concentrations of inhibitors $CuSo_4$ onto grafting using monomers (AAc and MAAc acid) at 30wt % and 20 kGy.

Figure (3): Study the effect of different concentration of inhibitor $CuSo_4$ onto grafting percent of LDPE using monomer concentration 30wt% MAAc, AAc at irradiation dose 20kGy, in case of MAAc it is clear that although the degree of grafting is high in 0.2wt% and more highest in 0.4wt%, the selected concentration is 0.06wt% since the produced film was more flexible and its shape is reasonable. This confirmed that there is specific ratio of the inhibitor which may permit to the free radicals to defuse interior to the polymeric substrate [36].

Effect of the Irradiation Dose onto the Grafting Percent:

Figure (4):Show the study of relationship between the degree of grafting and different irradiation dose(kGy) for monomer concentration (30wt% MAAc) onto LDPE film.It is seen that the degree of grafting increase as irradiation dos increase

however at 10 kgy produces a maximum grafting the reasonable film obtained at 20 kGy [5], this prove that the free radicals created by irradiation of polymers are immobilized, and may remain trapped for a period of time and subsequently the monomer is contacted with the irradiated polymer. The grafting yield obtained by this method usually depends on the efficiency of the trapped radicals. The main factor governing the trapping of radicals is the physical state of the irradiated polymer[5,40]. Also in case of (30wt% AAc) onto LDPE film it found that the degree of grafting is very high at 20 kGy but is highest more than at 15 kGy. but the reasonable film obtained at 20 kGy.

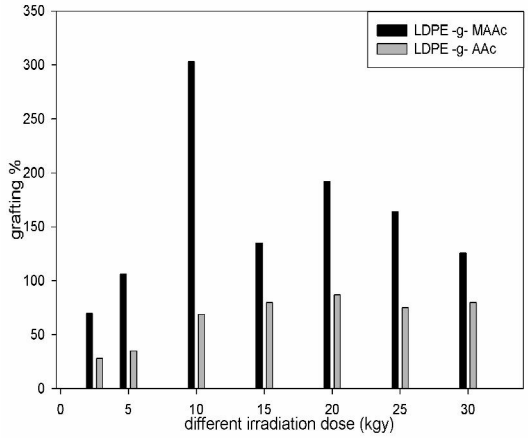


Figure (4): Effect the different irradiation dose onto (LDPE-g- AAc) and (LDPE-g-MAAc) at 30wt% of monomers and 0.06wt% of $CuSo_4$ as inhibitor.

Swelling Studies of Prepared Copolymers:

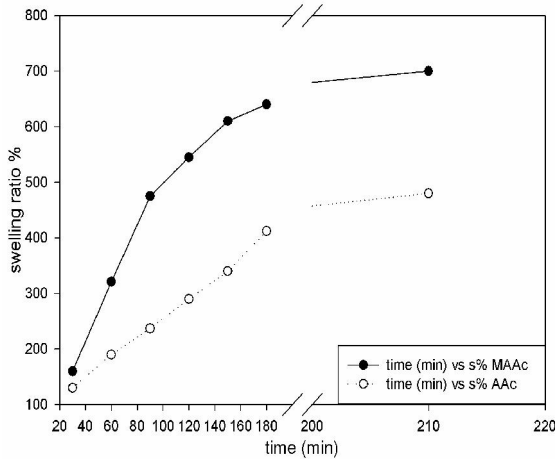


Figure (5): Effect of time (min) on the swelling ratio onto LDPE films using (AAc) and (MAAc) 30wt% at 20 kGy.

Figure (5): shown the study of swelling percent% at different time intervals (min) onto at irradiation dose 20Kgy and 30wt% of AAc and MAAc. It was observed that the LDPE-g- AAc and LDPE-g-MAAc films increases with increase the time (min).This is attributed to the increase in ionic monomer within the polymer matrix causes an enhancement in its swelling capacity due to increased chain relaxation[41]. Also, it seen that the swelling of LDPE-g-MAAc films increase more than the LDPE-g- AAc films which may be attributed to the monomer acrylic acid is ionic, its concentration may influence the swelling capacity or water uptake, This causes an enhancement in the chain relaxation owing to the repulsion among similarly charged–COO groups on the other hand, the relatively slower saturation of PAAc samples occurs on a distinctly higher level of swelling. The observed increase in the equilibrium water uptake with initial increase in the PAAc content may be attributed to the fact as the concentration of acrylic acid increases, the number of–COO groups along the macromolecular chains also increases along with increase in number of free H+ ions (counter ions) within the film phase. Moreover, higher concentration of free or mobile counter ions in the film phase. These two factors ultimately result in higher water uptake of films[41]. And the intra- and intermolecular hydrophobic inter actions in macro molecules of PMAA poly complex in the presence of alpha-methyl groups in PMAAc resulted in the higher hydrophilicity of PMAAc than PAAc[54,55].

Effect of Different pH

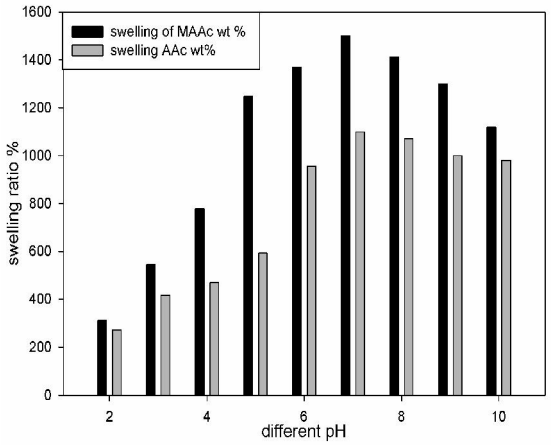


Fig (6): Effect of different pH on swelling ratio of LDPE films using (AAc and MAAc) monomers after 24 h and PH_7.

Figure (6): The effect of different pH on swelling ratio of LDPE films were investigated. It was found that when using monomer concentration of AAc and MAAc 30wt% the higher swelling ratio at Ph_7. The equilibrium swelling ratio in different pH buffer solutions swelled more at higher pH due to the electrostatic repulsion between the ionized forms of the carboxylic group, below a pH of 6.0, the swelling ratio drastically decreased, indicating that was in a

relatively collapsed state mainly due to the formation of hydrogen bonding. It is also interesting to note that the highest swelling ratio for a specific pH value and its value reached approximately 1560wt% at a pH_7. swelling coefficient with increasing AAc concentration due to availability of more carboxyl groups for ionization[42]. As a result, electrostatic repulsion increases along the chain, which causes an expansion of the chain [43,44]. Low swelling ratio at low pH is due to a high content of carboxylic acid groups that remain un-ionized at this pH. As the pH increases, swelling also increases due to ionization of carboxylic groups. However, it is interesting to see that swelling ratio of formulations with various concentration the number of carboxylate groups decreases, resulting in a decrease in the intermolecular repulsion forces, which leads to reduction of free spaces available for swelling [44,45].From the plot, it was observed a gradual increase in swelling ratios from pH 2.0 –7.0, and then a sharp transition is observed from pH 7.0–10.0 with a slight decrease in water uptake. Because the pKa of carboxylic acid containing in the copolymer is about 4.5, and carboxyl groups of hydrogels tend to dissociate at a pH > 4, the osmotic pressure inside the hydrogels increases resulting in a higher swelling. In the range of pH 7.0–10.0, the system has a basic pH and the concentration of basic cations in the outer solution also increases. As a consequence, the mobile ion concentration increases more rapidly than in the outer solution. Thus, a sharp transition was observed in this pH range. The decrease in swelling above pH 7.0 can be explained in that the –COOH groups may dissociate and further increase in the amount of mobile ions leads to a decrease in osmotic pressure [41].

Study the Drug Loading Amount to the Loading Time (min):

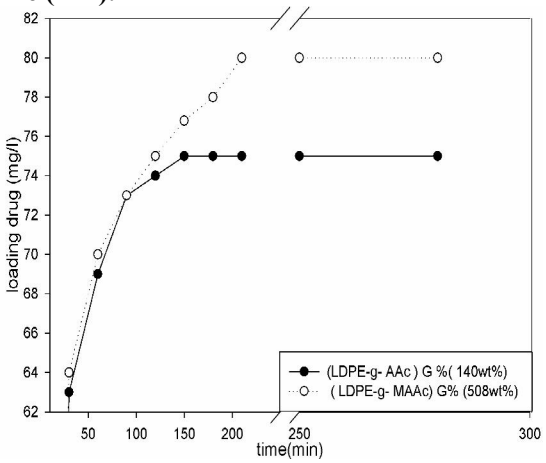


Figure (7): The dependency of drug loading amount to time (min) of (LDPE-g- AAc) G% (140wt %) and (LDPE - g- MAAc) G% (508wt%) in pH_7.

Figure (9): Show the study of the drug ciprofloxacin loaded onto (LDPE-g- AAc) films and (LDPE-g- MAAc) films were investigated.The concentration of ciprofloxacin drug loaded at selected time intervals was determined by (UV) spectrophotometer at specific pH $_7$ (distilled water). The drug (CPFX) was loaded at specific (pH_7) on to the (LDPE-g- MAAc) films. The degree of grafting of the film 508wt%, from figure shown that the degrees of drug loading ≥ 80 % at about time 250 min and after this time loading of drug tend to leveled off this agree with similar cases of study by the swelling – diffusion method. Also in case of (LDPE-g- AAc) films the degree of grafting of the film of 140 wt% as shown in figure the degree of drug loaded increase gradually until reach to 74% at about time 150 min and then begins leveled off [34]. The leveling of and steady stat of loading may be occurred due to for the (LDPE-g- MAAc) films and (LDPE-g- AAc) films were loaded by diffusion method through the three-dimensional network structure of chain of polymer matrix resulting in the initial burst [33] which may causes partial decrease in loading ratio of more drug in both polymers and also Ciprofloxacin contain(COOH) group which may be produce electrostatic forces which make reparation force effect in COOH group in AAc and this may be not occurred in MAAc which let incorporation of ciprofloxacin is high and easy to contact by methyl group of methacrylic acid grafted on the LDPE film so due to drug release of (LDPE-g-MAAc) higher than(LDPE-g- AAc) films [39].

The Effect of Time on the Release of Ciprofloxacin from (LDPE-G- AAc) and (LDPE-G- MAAc) As Function of Time:

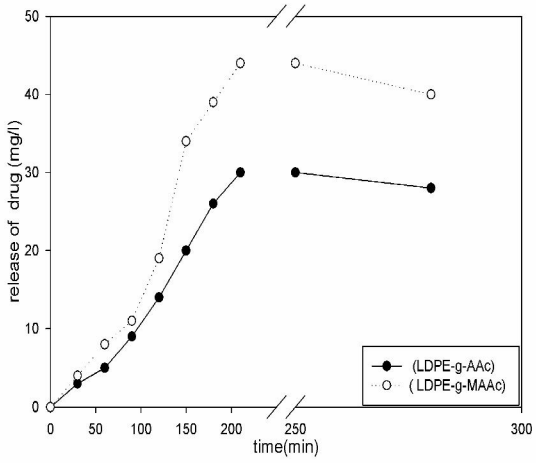


Figure (8): The dependency of drug release amount to time (min) of (LDPE-g- AAc) films were G% (140wt %) and (LDPE - g- MAAc) films were G% (508wt %) in pH_7.

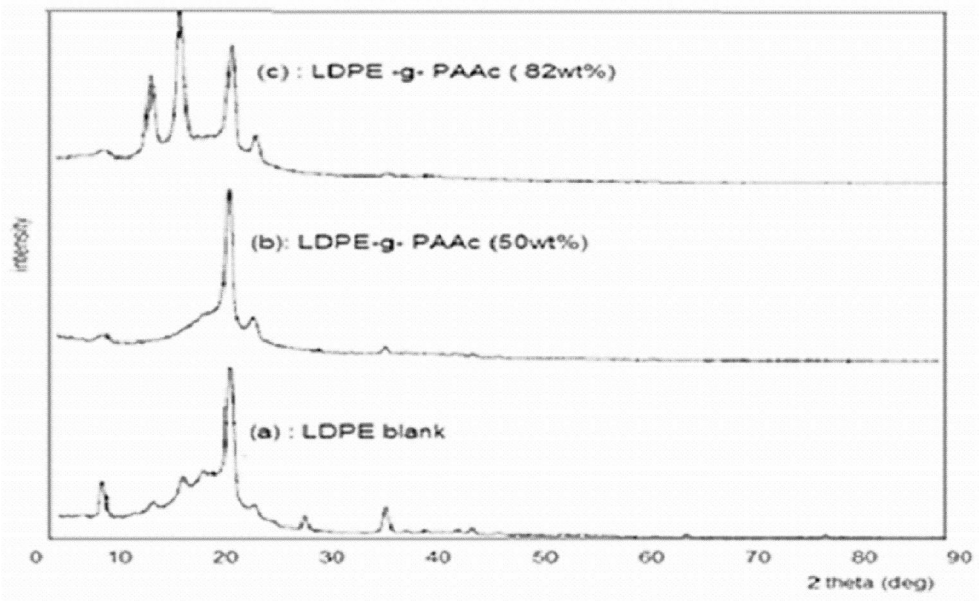


Figure (9) (a): Study the X- Ray Diffraction (XRD) for:- (a): LDPE blank.
(b): LDPE with monomer (PAAc) degree of grafting (50wt %).
(c): LDPE with monomer (PAAc) degree of grafting(82wt%).

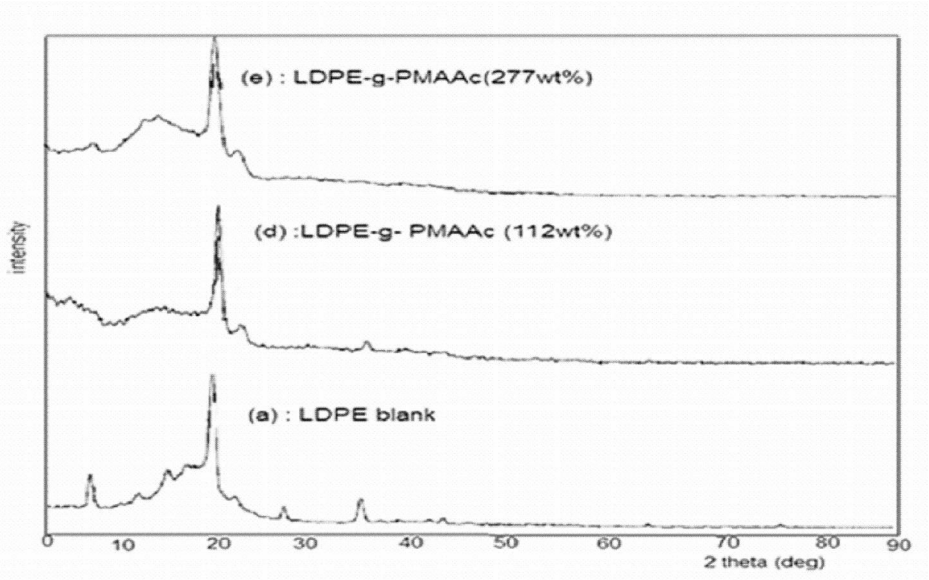


Figure (9): (b): Study the X- Ray Diffraction (XRD) for: - (a): LDPE blank.
(d): LDPE with monomer (PMAAc) degree of grafting (112wt %).
(e): LDPE with monomer (PMAAc) degree of grafting (277wt %).

From figure (8) it was found that the drug released (CPFX) was investigated. The drug was constantly released from the (LDPE-g-MAAc) films with the degree of grafting (508wt%) at pH $_7$ and could reach 44 % also (LDPE-g-AAc) films with the degree of grafting (140wt%) at pH_7 reached also 30 % at 250 min. However, the release content was comparatively high and then decreased slightly. The probable reason for the (CPFX) drug release from grafted films by diffusion through the three-dimensional network structure of the(LDPE-g-MAAc)and (LDPE-g-AAc) films, resulting in the initial burst [33,37] which may ceases a dissociation of drug molecules in the media. Also the % drug release of (LDPE –g- MAAc) that was showing higher drug release rate with respect to (LDPE –g- AAc). Due to poor linking with polymer matrix, drug easily comes out from grafted (LDPE -g- MAAc). But in case of (LDPE –g- AAc), drug is highly embedded in polymer

matrix due to crosslinking of polymer, results into slow release of drug from the polymer matrix [39].

X- Ray Diffraction (XRD) Measurements:

X- Ray Diffraction (XRD) is a fundamental technique in determining the crystal and amorphous of the grafted and un grafted film.XRD technique was performed to clarify the changes in morphological structure caused in polymeric substrates [36]. Figure (9 "A" "B") Show the XRD patterns for LDPE blank and their grafted films. LDPE graft copolymers prepared in different degree of grafting % there are mainly two crystalline peaks in the XRD patterns; one in the angular range (2θ of 18–22□4°) and another in the range 35□4–35□8°. This finding confirms the crystallinity of polyethylene, which corresponds to an orthorhombic unit cell. These peaks are well characterized in LDPE [5,46] There is The intensity of the crystalline peak of LDPE graft copolymers decreases with increasing degree of grafting and there is a noticeable broadening of the XRD peaks in the range 2θ = 35□4–35□8°for all the grafted films. These features are indicative of a reduction in the crystallinity of the LDPE with increasing degree of grafting [5]. from Figure (9) Show the XRD pattern it was found that the crystallinity peak for the blank and all grafted films occurs at the same angle (2*θ*) =18–22□4°, meaning that there is no change in the structure. However, the peak intensities of all grafted films are lower, and decrease with the increase in the degree of grafting. This means that the crystallinity decrease with the increase in the degree of grafting [47]. But in case of (d) PAAc is known as amorphous polymer. Wide-angle XRD showed similar diffraction pattern with ranging in between 18 and 20_, which indicated that the membranes were predominantly amorphous. From figure it seen that. two sharp diffraction peaks at 16_ and 22_ ensured its amorphous nature[48].These results suggested that the inherent crystallinity of the backbone polymer was not employed by the graft copolymerization of AAc and that the grafting occurred only in the amorphous regions [5,49,50].

FTIR Sepectroscopy (FTIR):

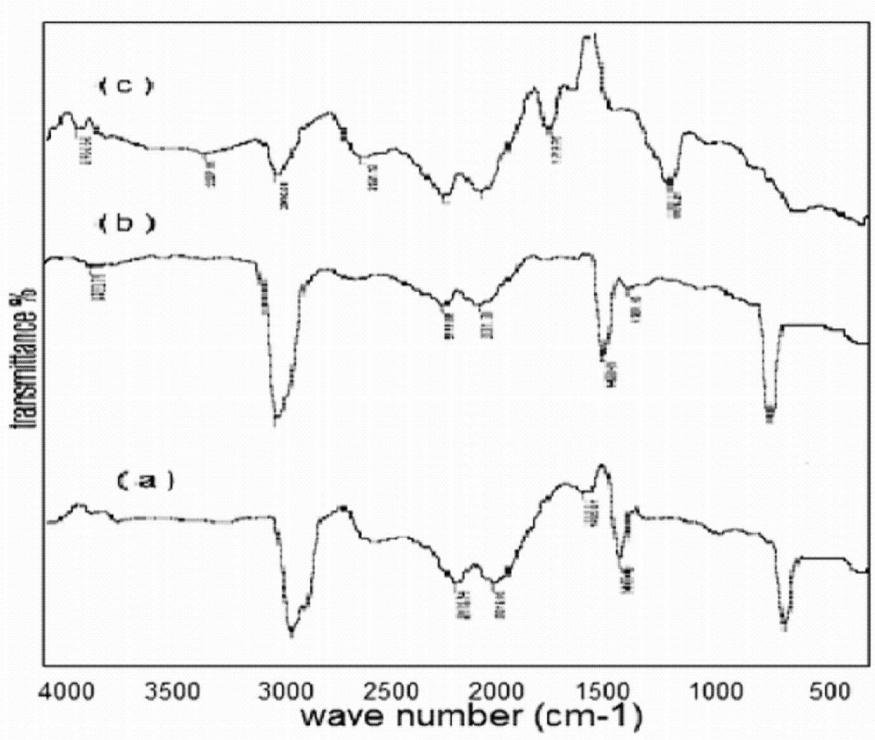


Figure (10 "A"): FTIR spectrum of (a) LDPE blank, (b) LDPE - g – AAc (28%)and (c) LDPE – g – AAc (75%

Figure (10 " A,B"): In order to confirm the surface structure of the grafted films, they were examined by FTIR The starting LDPE film has strong bands at 2930cm^{-1} and 2950cm $^{-1}$ due to CH_2 stretching, 1460 cm $^{-1}$ due to CH_2 bending and 720 cm^{-1} and1470cm^{-1} due to CH rocking. After grafting, the730 cm^{-1} spectra shows characteristic bands of LDPE blank. This leads to the exist in the grafted layer and (LDPE-g-AAc) were determined, the infrared analysis was based on the identification of absorption bands related to vibrations of functional groups present in the grafted films and non-existent in

LDPE blank.In fig (b) (LDPE-g-AAc) degree of grafting 28wt% no appear change on peaks about LDPE blank but the intensity of peak at 2011cm^{-1} and 2017cm^{-1} decreased and in fig (c) (LDPE-g-AAc) degree of grafting 75wt% these are the vibrations characteristics of the of the carbonyl group 1713 cm^{-1} with a characteristic shoulder at 1650 cm^{-1} and appear the peak at 3230cm^{-1} it is indicated that the presence of –OH group stretch. The films studied belong to the region where degree of grafting increases. In this region, one observes a continuous increasing of the peaks characteristic with increasing grafting. These results again seem to confirm that, grafted branches grow with increasing degree of grafting [26]. After grafting a new characterization peaks appears at 1713cm^{-1} which prove the incorporation of new change specific for AAc after irradiation grafting[52]. Also in fig (d) it is clear that the FTIR spectra of LDPE under different conditions of MAAc is expected to result in the presence of group and hence, the peak corresponding to this group expected to appear at 1670 cm^{-1} in the FTIR spectrum.Spectrum a corresponding to LDPE has a very small peak at 1670 cm^{-1}. Irradiated LDPE and (LDPE-g-MAAc) grafted degree 36wt%.Also in fig (e) exhibit sharp peaks at 1680 cm^{-1} indicating presence of carboxyl group. However, intensity of peak for (LDPE-g- MAAc) grafted degree 128wt%.is higher compared to that of irradiated LDPE[21]. The observation that peak appearing at 1680 cm^{-1} in spectrum of (LDPE-g-MAAc) is due to grafting of MAAc.

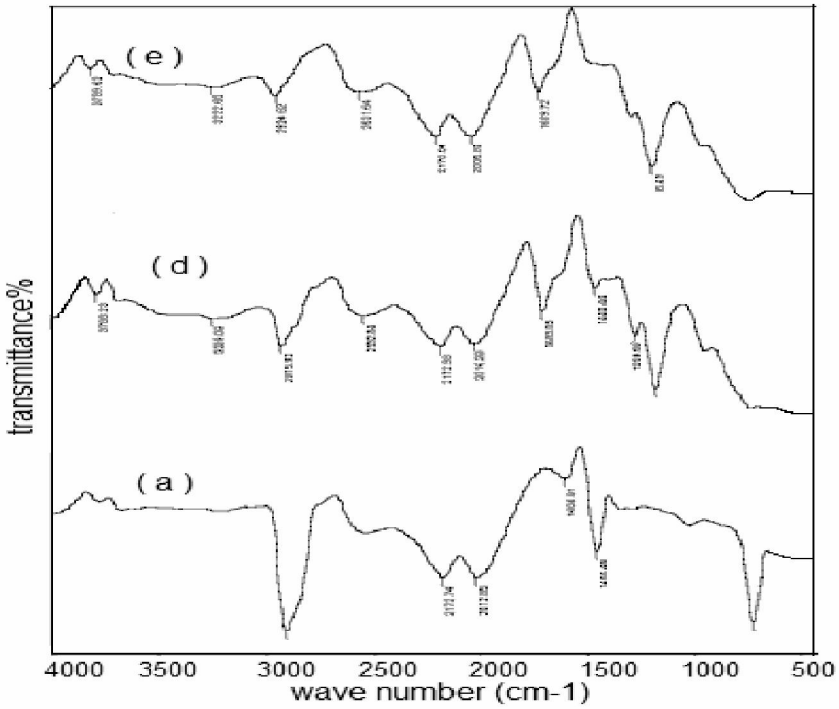


Figure (10"B"): FTIR spectrum of (a) LDPE blank,(d) LDPE – g – MAAc (36wt%) and (e) LDPE – g – MAAc (128wt%).

11.Scanning Electron Microscopy (SEM).

The morphological or topological changes of the LDPE films produced by radiation-induced graft polymerization have been directly investigated as shown in figure (11). The use of scanning electron microscopic techniques for these purposes illustrate, the distribution of the grafted poly mathacrylic acid (PMAA) chains on the surface of the LDPE film. also, it is clear that the LDPE surfaces before grafting is smooth and after grafting the added grafted chains are accumulated on the surface and the features shown in the images should originate from the local chemical contrast.

Compared to the surface of the control sample, there is an obvious increase in the toughens features on the grafted surface. It suggests an uneven distribution of graft chains on the LDPE film surface, which is in agreement with the previous research result that a degree of grafting causes an uneven distribution of graft chains on PE film surfaces [53]. Usually PMAA is distributed on the LDPE surface as granular formations when the degree of grafting is low, and when the degree of grafting is close to 100

wt%, the growing PMAA grains join together, and a compact coating with few defects is formed, whoever, the increase of graft percent increases the toughens on the surfaces due to the increase of grafting till 377 wt% on the film surface. The uneven distribution is favorable to clarifying the effects of radiation-induced grafting on the heterogeneous nucleation and growth of PMAA chains.

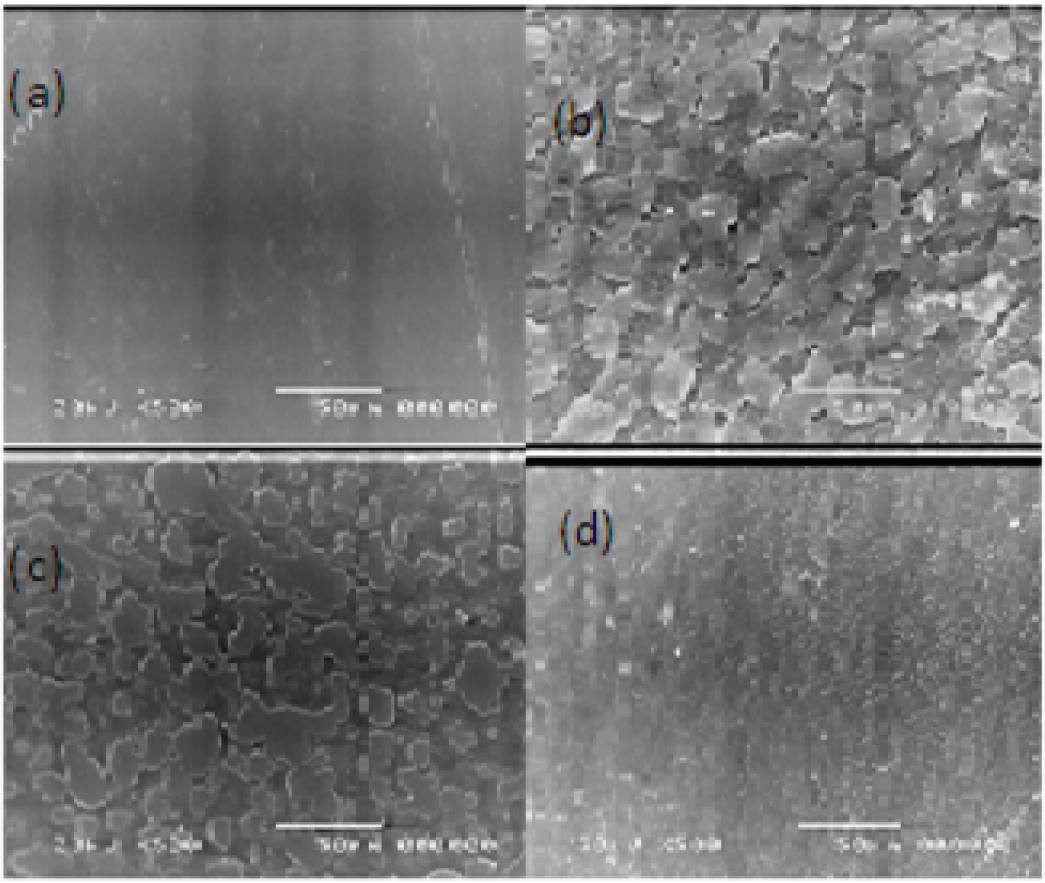


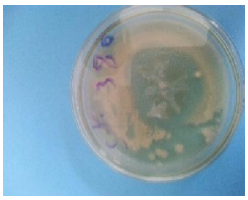
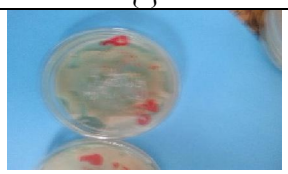
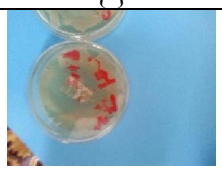
Figure (11): Study Scanning Electron Microscopy (SEM):
(a) LDPE blank.
(b) LDPE –g- MAAc (degree of grafting 97wt %).
(c) LDPE –g- MAAc (degree of grafting 226wt %).
(d) LDPE –g- MAAc (degree of grafting 377wt %).

12. Application Of Prepared Copolymergrafted film As Antimicrobial Active Polymer:

The synthesized polymeric grafted film, (LDPE-g- MAAc) and (LDPE-g- AAc) are tested for their antibacterial and antifungal activities. The synthesized polymeric grafted films were screened against selected microbial isolates, the yeasts, one Gm + ve bacteria and four Gm -ve bacteria. The results of the disk diffusion tests showed different degrees of growth inhibition. No antimicrobial activity against yeast strain under this study *Candida albicans*, *Saccharomyces cerevisiae* and *rhodotorula glutinis* is observed. The antimicrobial activity of the synthesized polymeric compounds, under study was evaluated based on the diameters of clear inhibition zone surrounding the polymeric substances. If there is no inhibition zone, it is assumed that there is no antimicrobial activity. As shown in Table (1).

It is clear that the inhibition activity with *Staphylococcus aureus* is very high however in case of polyethylene grafted PAAc has no response at all, Also, in case of *Escherichia coli there is a moderat* inhibition, and in case of *proteus sPP* the inhibition occurred by large amount in grafted of AAc more than in case of PMAA, however in cases of *Klebsiella pneumonia, Pseudomonas aeruginosa Salmonella typhi and Candida albicans* has no response. This proves that the prepared grafting copolymers can be applied as antimicrobial active materials.

Table (1): Shows the inhibition zone by the agar disc diffusion method of synthesized polymeric grafted film on the selected microorganisms.

Polymeric grafted film / **Name of Isolates**	(LDPE-g- MAAc) **film the degree of grafting (380wt %)**	(LDPE-g- AAc) **film the degree of grafting (72wt %)**
Staphylococcus aureus	 {+ +}	{+++}
Escherichia coli	 {++}	 {+++}
Klebsiella pneumonia	{-}	{-}
Pseudomonas aeruginosa	{-}	{-}
***P*roteus spp**	 {-}	 {+++}
Salmonella typhi	{-}	{-}
Candida albicans,	{-}	{-}

Conclusion:

The radiation induced graft copolymerization by the simultaneous method is a promising method that provides a suitable and economical technique to graft (AAc, MAAc) monomers onto LDPE. Radiation is useful to prepare and modify polymers, because firstly, it does not need any catalyst or initiator, so it is suitable to obtain products with high purity and secondly, for the high energy of radiation. The preparation of grafted films occur (in the presence of cupper sulphate as inhibitor) and environmental conditions play important role for grafting as monomer concentration, irradiation dose, inhibitor type and concentration of inhibitor. This study produced affinity grafted polymer film using the optimum the grafted percent occurred at 30wt% AAc and 50wt% MAAc however the reasonable grafted film obtained at also 30wt% MAAc. The maximum grafting occurred using cupper sulphate than other inhibitor and the optimum $CuSo_4$ ratio was 0.06 also the maximum degree of grafting 10 kGy for MAAc and 20 kGy for AAc. Study of swelling percent shown maximum swelling at time after (24 h) by the ratio 400% for AAc and 600% for MAAc.The effect of pH study prove that pH_7 is specific pH which undergo the maximum ratio for swelling.The characterization of prepared grafted copolymer have been investigated XRD and it prove that the crystallinity peak for the blank and all grafted films occurs at the same angle (2θ) =18–22□4°and the peak intensities of all grafted films are lower and decrease with the increase in the degree of grafting and increase of AAc at two sharp diffraction peaks at 16_ and 22_ ensured its amorphous nature of AAc which prove that the inherent crystallinity of the backbone polymer was not employed by the graft copolymerization of AAc and that the grafting occurred only in the amorphous regions.

References:

1. Maykel González Torres, Jorgecerna Cortez, Manuel González Pérez, Rogelio Rodríguez Talavera, International Journal Of Science And Advanced Technology 2, (9), Pp. 2221-8386, (2012).

2. Pınar Akkas_ Kavakl, Cengizkavaklı, Noriakiseko, Masao Tamada, lgungu ¨Ven, Nuclear Instruments And Methods In Physics Research, 265, Pp. 204-207, (2007).
3. Seko N., M. Tamada, F. Yoshii, Nucl. Instr. Meth. Phys. Res. Vol. 21,Pp.236, (2005).
4. Zaureshs.Nurkeeva,A.-S.Abdelaala, Anatoliyi. Kupchishin, Vitaliyv. Khutoryanskiya, Grigoriya. Mun, Aida G. Beksyrgaeva, Radiation Physics And Chemistry 68,Pp. 793–798, (2003).
5. MADANI M, Bull. Mater. Sci. Vol. 33, No. (1), Pp. 65–73, (2010).
6. Chen J, Asano M, Yamaki T And Yoshida J. Membr. Sci.Vol.38, Pp. 256,(2005).
7. Billmeyer F W In Textbook Of Polymers Science (Newyork: John Wiley & Sons Inc),(1984).
8. Benson R S Nucl. Instrum.Meth.Vol.5, Pp.191 - 752, (2002).
9. Ferreira L M, Falcao A N And Gil M H Nucl. Instrum, Meth. Pp.236 -513,(2005).
10. Emilio Bucio and Guillermina Burillot, Radiat. Phys. Chem., Vol. 48, No.(6), Pp. 805-810, (1996).
11. Guthrie J.T., Surf. Coat. Int. Part B: Coat. Trans. Vol.85, Pp.1- 27,(2002).
12. Paik H.J., S.G. Gaynor, K. Matyjaszewski, Macromol. Rapid Commun. 19, (1),Pp. 47, (1998).
13. Hawker C.J., D. Mecerreyes, J. Dao, J. Hedrick, I. Barakat, P. Duboise, R. Jerome, W. Volkson, Macromol. Chem. Phys. Vol.198, No. (1), Pp.155, (1997).
14. Miwa Y., K. Yamamoto, M. Sahaguchi, S. Shimada, Macromolecules Vol.32,Pp. 8234 (1999).
15. Stehling U.M., E.E. Malmstron, R.W. Waymouth, C.J. Hawker, Macromolecules,Vol. 31, Pp.43-96, (1998).
16. Singh S.K. A, S.P. Tambe, A.B. Samui, V.S. Raja, Dhirendra Kumar, Appl. Polym. Sci.Vol. 27, Pp.1033, (1999).
17. Kabay, N.; Katakai, A.; Sugo, T.; Egawa, H. J Applpolymsci,Vol. 49,Pp. 599, (1993).
18. Ferreira L.M., A.N. Falca˜o, M.H. Gil, Nuclear Instruments And Methods In Physics Research B, Vol. 236, Pp. 513–520, (2005).
19. Gupta B. D. And Chapiro A Preparation Of Exchange Membranes By Grafting Acrylic Acid Into Pre-Irradiation Poly Mer Films. Grafting Into Polyethylene. Eur. Polym. J.Vol. 25, No.(11), Pp.1137, (1989).
20. Ishigaki I., Sugo T., Senoo K., Okada T, Okamoto J. And Machi S. Graft Polymerization Of Acrylic Acid Onto Polyethylene Film By Preirradiation Method. Part I. J Appl. Polym. Sci. Vol. 27, Pp.1033, (1982).
21. Sidorova L. P., Aliev A. D., Zlobin V. B., Aliev R. Echalykh A. E. And Yakabanov V. Modificationof Polyethylene by Radiation-Induced Graft Polymerization of Acrylic Acid. Radiat. Phys. Chem. Vol. 28, No. 4, Pp.407, (1986).
22. Ishigaki I., Sugo T., Senoo K., Okada T,, Okamoto J. Andmachi S. Graft Polymerization Of Acrylic Acid Ontopolyethylene Film By Preirradiation Method. Part I. J. Appl. Polym. Sci. Vol. 27,Pp. 1033, (1982).
23. Kaji K. Distribution Of Grafted Poly(Acrylic Acid) Inpolyethylene Film. Journal Appl. Polym. Sci. Vo. 32, Pp.4405,(1986).
24. Charlesby A. Andfydelor P. J. Preliminaryobservations On A New Class Of Sensitizers For Cross Inkingpolyolefins. Radiat. Phys. Chem. Vol. 4,Pp. 107, (1972).
25. Chapiro A. Radiation Chemistry Of Polymericsystems. Interscience, New York, (1962). [26] Ferreira L.M. A, A.N. Falca˜o A, M.H. Gil B, Nuclear Instruments And Methods In Physics Research B, Vol. 236,Pp.513–520, (2005).
26. Yahya H. F. Al-Qudah1, Arab Journal Of Nuclear Sciences And Applications, Vol.45, No. (2), Pp.179-185, (2012).
27. Pappas, N.A.; Sahlin, J.J. Hydrogel As Mucoadhesive And Bioadhesive Materials: A Review Biomaterials, Vol. 17, Pp.1553–1561, (1996).
28. Khan, I.U.; Serra, C.A.; Anton, N.; Vandamme, T. Continuous-Flow Encapsulation Of Ketoprofen In Copolymer Microbeads Via Co-Axial Microfluidic Device: Influence Of Operating And Material Parameters On Drug Carrier Properties. Int. J. Pharm., V.441, No.(1-2),Pp. 809-817, (2013).
29. Kashif Sohail1, Ikramullah Khan, Yasser Shahzad, Talib Hussain4, Nazar Muhammad Ranjha, Brazilian Journal pharmaceutical Sciences Vol. 50, No. (1), Pp. 173-184,(2014).
30. Li Zhi Wu Songliang Yang Xiangmin Zhang Weidong Yang Cunzhong Fang Bin Xie Pengfeinuclear Science and Techniques,Vol. 24, Pp. 15-20, (2013).
31. Dessouki, A.M., El-Tahawy, M., El-Boohy, H., El-Mongy, S.A., Badawy, S.M., Chemical Reactive Paper Prepared By Radiation-Induced Graft Copolymerisation-I. Radiat. Phys. Chem. Vol. 54,Pp.627–635, (1999).
32. Tao J. And Ping H. Radiation-Induced Graft Polymerization Of Isoprene Onto Poly hydroxyl

butyrate. Polymer Journal. 33(9),P(647- 653), (2001).
33. Langenbach M.R., J. Schmidt And H. Zirngibl, Surg. Endosc., Vo.l 17, Pp. 1105, (2003).
34. Dalia E. Hegazy, Journal Of Chemical Engineering Vol. 1, No. (1), Pp.42-46, (2012).
35. Nabila Mahmud Mazyad, Thesis, Preparation Of Polymeric materials By Radiation For Different Industrial Waste Treatment, (1997).
36. Kathah, A. A., Burford, R. P.Rind Garnett, J. L. Rudinf. Phys. Cheer. Vol.39, No. (3), Pp.293-302, (1992).
37. Vahidhaddadi-Asl, Robert P.Burford And John L. Garnett,Airanian Journal Of Polymer Science And Technology, Vol. 4, No.(1), Pp.170-179, (1995).
38. Colombo P, Santi P, Bettini R, Brazel CS, Peppas NA. Drug Release From Swelling-Controlled Systems. In: Wise DL, Brannon-Peppas L, Klibanov AM, Langer RS, Mikos AG, Peppas NA, Trantolo DJ, Wnek GR, Yaszemski MJ, Editors. Handbook Of Pharmaceutical Controlled Release Technology. New York: Dekker, Vol.10, Pp. 183–209, (2000). Chen, L. Yang, Y.C. Nho And A.S. Hoffman.
39. J. Topics In Tissue Engineering, Vol. 4, Pp.15-20, (2008).
40. Seddiki Nesrinne, Aliouche Djamel, Arabian Journal Of Chemistry, Vol.5, Pp.15-20, (2013).
41. Hongyan He, M.S, Thesies, Multifunctional Medical Devices Based On Ph-Sensitive Hydrogels For Controlled Drug Delivery,(2006).
42. Jin, L.; Lu, P.; You, H.; Chen, Q.; Dong, J. Vitamin B12 Diffusion And Binding In Crosslinked poly(Acrylic Acid)S And Poly(Acrylic Acid-Co-N-Vinyl Pyrrolidinone)S. Int. J. Pharm., Vol.371, No.(1-2), Pp.82-88, (2009).
43. Kashif Sohail1, Ikramullah Khan, Yasser Shahzad4, Talib Hussain4, Nazar Muhammad Ranjha1, Brazilian Journal Of Pharmaceutical Sciences Vol. 50, N. (1), Pp.173-184, (2014).
44. El-Hag, A.A.; Shawky, H.A.; Abd El Rehim, H.A.; Hegazy, E.A. Synthesis And Characterization Of Pvp/Aac Copolymer Hydrogel And Its Applications In The Removal Of Heavy Metals From Aqueous Solution. Eur. Polym. J., Vol.. 39, No.(12), Pp.2337-2344, (2003).
45. Chattopadhy S, Bhowmick A K J.Appl ploym. Sci. Vol.81, Pp.1936,(2001).
46. Li Zhi Wu Songliang Yang Xiangmin Zhang Weidong Yang Cunzhong Fang Bin Xie Pengfei, Nuclear Science and Techniques Vol. 24, Pp. 20-25, (2013).
47. Anup Das, Sourabh Ghosh, Alok R. Ray. Polymer Vol. 52, Pp. 3800-3810,(2011).
48. Hegazy E A, Kamal H, Abdel Geleel M And Abdel Maksoud A J. Appl. Polym. Sci., Vol.5, Pp.10, (2005).
49. Toi K, Igarashi K And Tokuda T J. Appl. Polym. Sci. Vol. 20,Pp.703,(1976).
50. Kaji K. Distribution Of Grafted Poly(Acrylic Acid) In Polyethylene Film. Journal Appl. Polym. Sci. Vol. 32,Pp. 4405, (1986).
51. Tidjani A., R. Arnaud, J. Polym. Sci. Part A: Polym. Chem.Vol. 31No.(1), Pp.603,(1993).
52. Sidorova L. P., A. D. Aliev, V. B. Zlobin, R. E. Aliev, A. Chalykh and V. Y. Kabanov, Radiat. Phys. Chem., 1986, 28, 40.
53. Abdiyev, K.Z., Shaikhutdinov, E.M., Zhursumbaeva, M.B. Effect Of Polymer Concentration On The Surface Properties Of Polyacid-Poly(N-Vinylpyrrolidone) Complexes. Coll. J. Vol.65, No.(4), Pp.437–440, (2003).
54. Bo Deng, Yang Yu, Bowu Zhang, Xuanxuan Yang, Linfan Li, Ming Yu, Jingye Li A Radiation Physics And Chemistry,Vol. 80, Pp.159–163, (2011).

3/14/2015