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Grafting Copolymerization of Sodium Alginate/ Acrylic Acid/ Methacrylic Acid by Gamma Radiation: Preparation and Characterization

H.M.M. Abo Eldahab[a]*, R.S. Hassan[a], F.A. Shehata[a], S.A.El-Reefy[a], S.A.Mohamed[b]

[(a)] *Analytical Chemistry Department, Hot Laboratories and Waste Management Center, Atomic Energy Authority, Cairo, Egypt*
[(b)] *Chemistry Department, Ain Shams University, Cairo, Egypt*

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ABSTRACT

Grafted copolymer (sodiumalginate (Na. Alg)- acrylic acid (AcA)–methacrylic acid (MAcA)) was prepared by the gamma irradiation-induced copolymerization in the presence of N, N-methylene bis-acrylamide (MBA) as aco monomer crosslinker. The functionality, morphology and thermal stability of the prepared copolymer have been examined using FTIR spectroscopy, SEM, and TGA-DTA, respectively. The prepared material shows a smooth surface and relatively homogeneous appearance which reveals incompatibility between the monomers used. Thermal analysis of the prepared material shows stability near 400°C. The effect of the preparation conditions on the swelling property of the prepared copolymer has been investigated and the mechanism of grafting copolymerization through the irradiation process has been also discussed. The obtained results revealed that the optimum conditions for preparing a suitable grafted copolymer were using 20% Acrylic acid, 10% Methacrylic acid and 0.4 wt% sodium alginate at an irradiation dose of 15 kGy with the addition of 0.03 % of MBA as a crosslinker.

1. INTRODUCTION

Polymers as sorbent materials have found particular importance in the preconcentration and treatment of liquid waste [1]. Since they are characterized by having ionic and complex- ability nature, polymers showed affinity towards certain ions or groups of ions from solutions. The polymers should be characterized by adaptability (non-toxicity and non-antigenicity), biodegradable and biocompatible.

The application of natural resources in the preparation of polymers showed considerable advantages since they possess the potential for substitution of chemical materials [2]. The most common natural materials used in the preparation of polymers are gelatin, albumin, chitosan and sodium alginate[3]. As one of the natural materials, sodium alginate (NaAlg) is a linear polymer water-soluble salt of alginic acid. It is a naturally occurring heteropolysaccharide, extracted from natural brown algae [4]. Sodium alginate can be easily modified by different chemical or physical methods such as grafting copolymerization with other hydrophilic monomers such as acrylic acid [5].

The radiation-induced grafting copolymerization (RIGC) is one of the most acceptable methods for the preparation of polymeric materials of a wide range of properties. In this method, acceptable properties of the grafted copolymer can be obtained by choosing the appropriate pair or more of monomers and by controlling the conditions of the grafting process [6]. It is known that the grafting process by high energy radiation such as γ-rays improves the properties of polymeric materials [7-8]. In this concern, when the radiation from a γ-rays source interacts with a polymer, its energy absorbed by the polymeric material and active sites such as free radicals are produced, which in turn initiates the occurrence of different chemical reactions to occur [9-10].

Corresponding author: heba_mostafa2@yahoo.com
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The aim of the present work is the preparation and characterization of a novel copolymer based on using sodium alginate as a natural monomer and RIGC technique. The prepared grafted copolymer is characterized by FTIR, SEM, TGA to investigate its molecular structure, morphology, and thermal stability. Some other selected properties of the prepared grafted copolymer will be investigated and discussed to elucidate the possibility of its further use as a sorbent material.

2. MATERIAL AND METHODS

2.1. Materials

Sodium alginate (Na. Alg) was purchased as an alginic acid sodium salt (Fluka Chemie). Acrylic acid (AcA) and methacrylic acid (MAcA) were purchased from Sigma-Aldrich. The dissolution process was performed using de-oxygenated double distilled water which was bubbled by purging pure nitrogen gas at 80°C.

2.2. Preparation of Grafting Copolymer

A general procedure for grafting copolymerization of Acrylic acid (AcA) and methacrylicacid (MAcA) onto sodium alginate (Na Alg) backbone with methylene bisacrylamide (MBA) as acrosslinker using gamma irradiation technique was conducted as follows, unless otherwise stated:0.4 wt % sodium alginate was dissolved in degassed, distilled water, following this, 20 mass%(AcA) and 10 mass%(MAcA) were added to the total solution. 0.03mass% MBA as a crosslinker was added to the reaction mixture then shaken overnight in a glass tube, after that it was subjected to Co-60 gamma-rays irradiation (15kGy). The irradiated product (grafted copolymer) was cut into small pieces and washed by acetone for removal of excess of unreacted monomers[11], washed with double distilled water and dried in an oven at 80 °C and weighed. It is worthy to mention that in case of using some other conditions, no complete formation of the uniform polymer was obtained.

2.3 Gamma Irradiation

The irradiation process was carried out using the Co-60 gamma cell. A cell of type MC-20 (Russia) was used at the Cyclotron Project, Inshas site, Egypt. The monomers were exposed to different doses of gamma radiation (5-30)kGy. Gamma radiation leads to the formation of free radicals, so it acts as an initiator for the polymerization process. These free radicals are active sites that crosslinked with other monomers to get the grafted copolymer.

2.4 Characterization of the PreparedGrafted Co-polymer

2.4.1 Swelling studies

The swelling property was studied to explain the behavior of the prepared grafted copolymer in water. Swelling was carried out on all samples according to ASTM D4318, 2010 and ASTM D4546, 2008 standards, respectively. Accordingly, the dried grafted copolymer was immersed in distilled water until it swelled to equilibrium. In this respect, a known dry weight (W_i) of the grafted copolymer (50 mg) was immersed in a known volume of distilled water (10 ml) for 24 hours at room temperature. Swollen gels were removed from the water, dried with filter paper, and weighed (W_f). The swelling percentage (%S) of the gel was calculated from the following equation[12].

$$\%S = \frac{(Wf - Wi)}{Wi} 100 \quad \text{.....(1)}$$

Where W_i is the weight of the polymer in the dried state and W_f is the weight of the swollen polymer**.**

2.4.2 FTIR Spectroscopic analysis

FTIR (Fourier transformed infrared) spectrum of the copolymer was recorded by the LARA213 FT-IR spectrometer using KBr salt to form a disk and performed on a computerized spectrophotometer in the range of 4000-500 cm^{-1}.

2.4.3 Thermal analysis

TGA and DTA measurements were carried out using a Shimadzu thermogravimetric analyzer model TGA-50 (Tokyo, Japan). The thermal stability was investigated at a heating rate of 10°C/min, under nitrogen atmosphere (20 ml/min) from room temperature up to 600°C.

2.4.4 Scanning Electron Microscope (SEM)

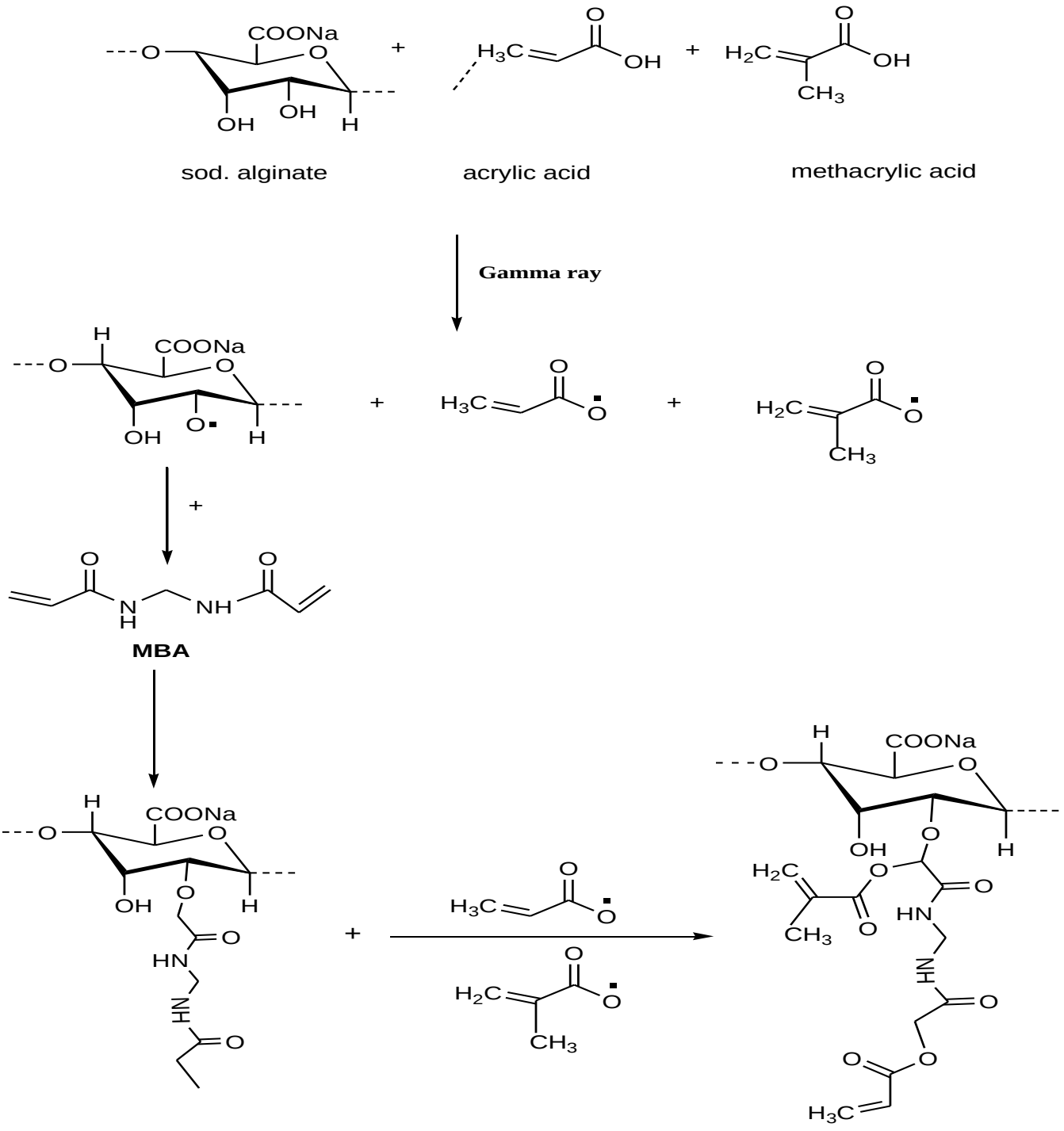
The surface morphology of the prepared polymer was examined by JEOL-JSM 6510 LA (Japan) and used for investigation of the pore structure at high magnification of an electron beam.

3. RESULTS AND DISCUSSION

3.1. Predicted Mechanism for Polymerization Process

Sodium alginate is known to contain a large number of free hydroxyl (OH) and carboxyl (COOH) groups along its polymer backbones which enables it to be easily modified [13]. Meanwhile acrylic acid and

methacrylic acid monomers have one active double bond and carboxyl hydrophilic groups that are easily binding with hydroxyl groups of water molecules to form hydrogen bonds. Accordingly, when acrylic acid and methacrylic acids are irradiated in the presence of NaAlg solution and MBA (crosslinker), the reaction between monomers occurs. It means that acrylic acid and methacrylic acid are anionic weak electrolytes, and have carboxylic acid groups which could develop different intermolecular interactions including electrostatic interaction, hydrogen bonds, and dipole-ion with other materials. Possible mechanism reactions for the graft polymerization of Na Alg/AcA/MAcA in the presence of an MBA can be predicted [14] **as shown in Scheme (1)**



Scheme (1): Possible mechanism reactions for the graft polymerization of Na Alg/AcA/MAcA in presence of MBA

3.2. Factors Affecting the Swelling percentage of the Prepared Co-polymer

The swelling property of the prepared copolymer is one of the most affecting parameters that should be studied to identify its physical and chemical behavior especially the hydrophilic property. The main factors that influence the swelling percentage of the prepared polymer include the following:

3.2.1 Effect of irradiation dose on swelling percentage

The effect of different gamma irradiation doses from 5.0 to 30 kGy on the swelling percentage of the prepared grafted copolymer was studied. The result obtained showed that using irradiation doses from 5-10 kGy was found to be not enough for complete polymerization. Accordingly, the effect of irradiation doses from 15-30 kGy on the swelling percentage was studied as shown in Fig. (1).It is clear from this Figure that the swelling % decreases with increasing the irradiation doses. This is due to the increase in amount (density) of crosslinked network structure at higher irradiation doses [15]which may cause compaction of the copolymer. Therefore, the irradiation dose was fixed at 15 kGy as it is sufficient for the polymerization process.

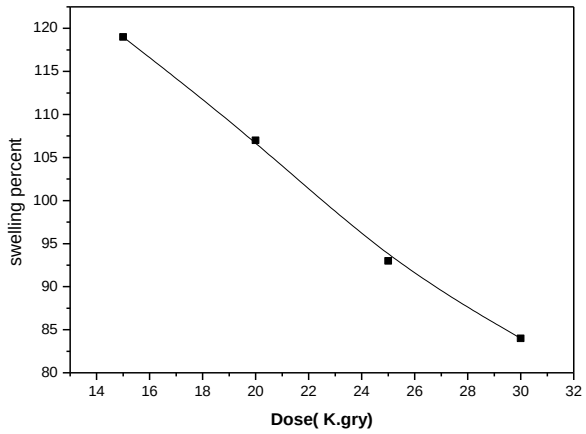


Fig. (1): Influence of the irradiation dose on the swelling percentage

Increasing the gamma radiation, the crosslinking of the matrix increased due to generation of free radicals and the swelling degree decreased. Increasing the gamma radiation and crosslinking at specific limit made the prepared polymer compact or inert material.

3.2.2. Effect of crosslinker concentration on swelling percentage

The effect of adding different concentrations of MBA, as a chemical crosslinker, ranged from 0.01 to 0.06 mass % on the swelling percentage was studied. This was conducted at a total monomer concentration of 30 mass % (20% AcA and 10% MAcA) and 0.4wt% NaAlg with an irradiation dose of 15.0 kGy. The results shown in Fig. (2) demonstrated that the swelling percentage decreases with increasing the concentration of the crosslinker. The decrease can be attributed to the higher increase in crosslinking with the polymeric chain which may cause a decrease of diffusivity of water through the network structure and a shrinkage of the polymer may occur[16].Therefore, the concentrations of MBA was fixed at 0.03 wt% which it is quite sufficient for polymerization without causing polymer shrinkage.

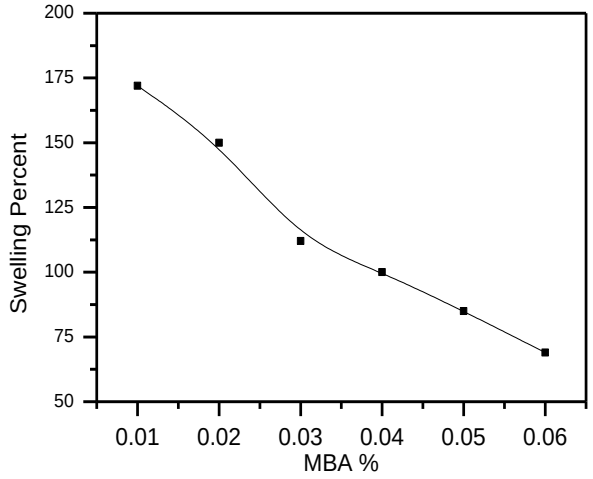


Fig. (2): Influence of the MBA concentration on the swelling percentage

3.2.3. Effect of sodium alginate on swelling percentage

Sodium alginate concentration plays an important role in the formation of (NaAlg/AcA/MAcA) polymer. The effect of different concentrations of sodium alginate from o.1 - 1 wt% on the swelling percentage of the prepared copolymer is given in Fig. (3). It is observed from this Figure that increasing NaAlg concentration leads to the increase in water uptake of the copolymer up to 0.2wt% of alginate and then it decreases to 1%. It is reported that the introduction of a hydrophilic polymer such as sodium alginate in the gel network of the copolymer increases its water absorption properties[17]. Besides, it also provides electrostatic repulsive force in the network because of its negatively charged carboxylate functional groups (COO^{-}). On the other hand, a further increase of NaAlg above 0.2wt% shows a decrease in the swelling percentage which may be due to filling up of the void spaces of the network chains by excess alginate [18-20].

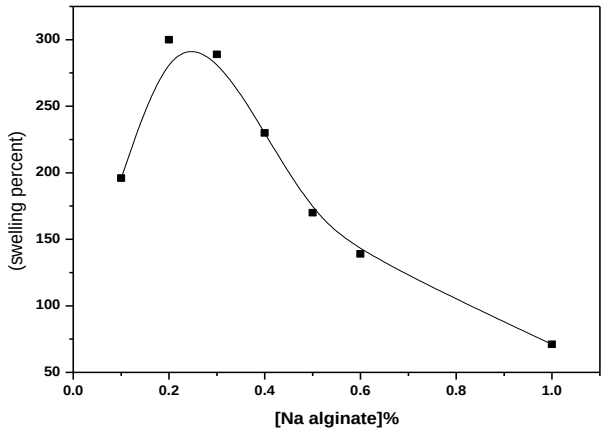


Fig. (3): Influence of the sodium alginate concentration on the swelling percentage

3.2.4. Effect of pH on swelling Percentage

The swelling percentage of the prepared copolymer was studied at various pH values ranged from 1.0 to 13.0. The obtained data revealed that at low pH values, the swelling percentage increases slightly with an increase in pH values as shown in Fig. (4). This is because COO^- groups of Na Alg can be converted to –COOH groups in the acidic solution causing a formation of a hydrogel bonding among –COOH groups of Na Alg and AcA which leads to an increase in the swelling percentage [22-23]. On the other hand, at high pH values, the carboxylic groups are converted to carboxylate anions with an expansion of the gel network due to electrostatic repulsion which results in a relative increase of swelling percentage [24].

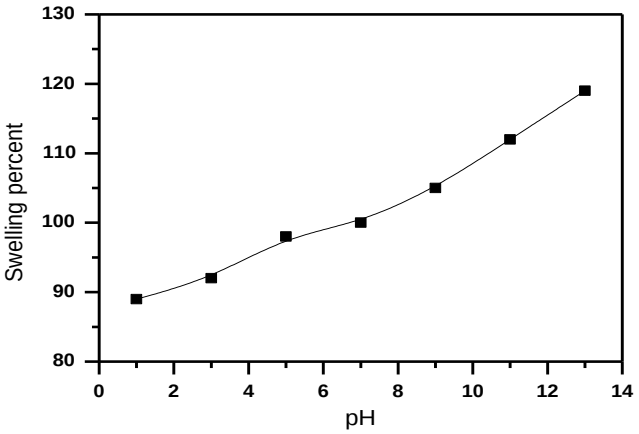


Fig. (4): Effect of pH on swelling percentage

3.3 Characterization of the Prepared Co-polymer

3.3.1. Scanning Electron Microscope:

SEM is important to clarify the topography (texture/surface) of a sample, morphology (Size, shape) and approve the compatibility of the monomers. The surface morphology of the prepared grafted copolymer is shown in Fig. (5). The prepared copolymer has a smooth surface and relatively a homogeneous appearance[25]. This indicates an increase in the compatibility between the used constituents.

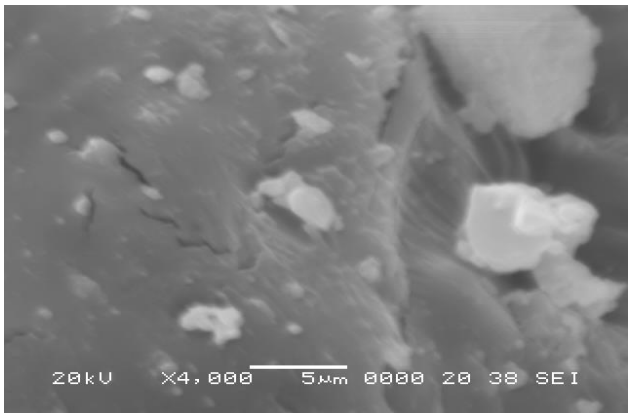


Fig. (5): SEM image of prepared grafted copolymer

3.3.2. Thermogravimetric analysis

Fig.(6) shows the thermal decomposition of the prepared grafted polymer. The degradation passes in three stages. The first stage from 50 to 170°C which shows that at 170°C exhibits a weight loss of 5.819 % with an endothermic peak, which may be due to the removal of absorbed water molecules[26]. The second stage from 170 to 330°C with endothermic peaks at 216.57°C exhibits a weight loss of 41.465%, which may be due to the release of COOH, water, and NH_3[27]. The third stage from 330 to 600°C, shows endothermic peaks at 524.69°C which exhibits a weight loss of 36.186 %, which may be due to the removal of volatile hydrocarbons and complete degradation to the oxide form [28]. The results showed that the polymer possesses thermal stability until near 400°C.

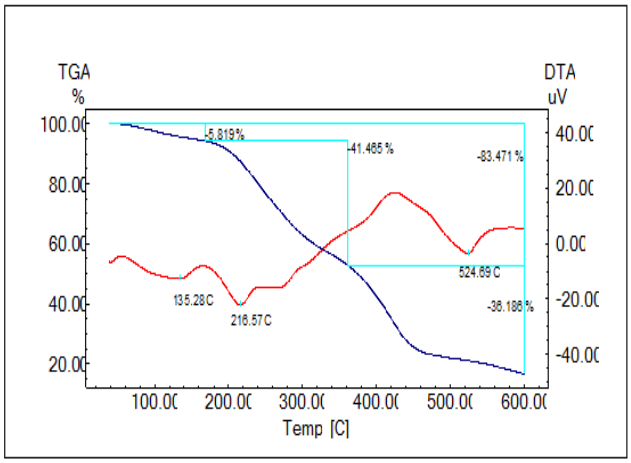


Fig. (6): Thermal analysis of prepared grafted copolymer

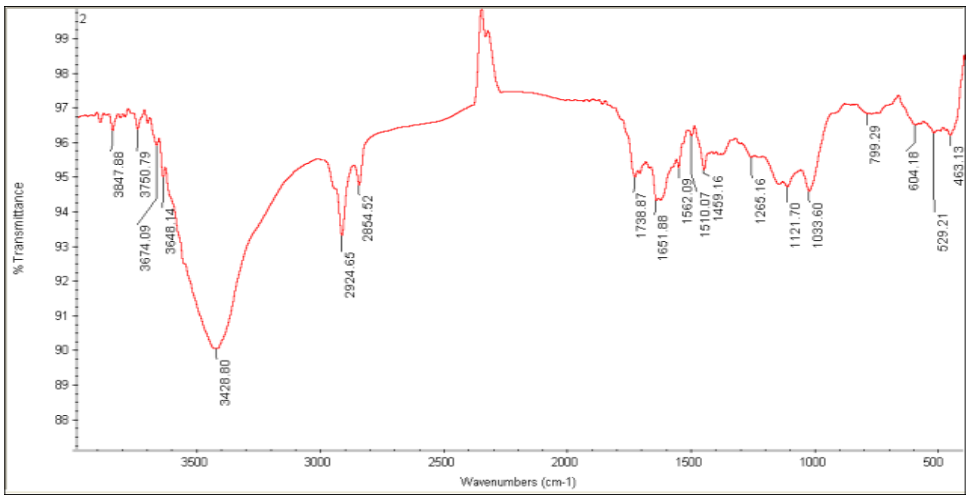


Fig (7): FTIR of the prepared polymer

3.3.3. FTIR spectra

FTIR spectroscopy was studied to identify the functional groups of the prepared grafted copolymer (Fig. 7).From literature, the FTIR of sodium alginate showed characteristic absorption bands of hydroxyl, ether and carboxylic functional groups, stretching vibration of O-H bands appeared in the range of 3600-3000 cm^{-1}. Stretching vibration of aliphatic C-H was observed at 2920-2850 cm^{-1}[29] and a stretching band of the carbonyl group C=O at 1750 cm^{-1}. Two peaks at 1649 and 1460 were attributed to COO(asymmetri-c)and COO(symmetric) groups, respectively. The FTIR spectrum of sodium alginate also shows a strong broad peak between 1107 and 935 cm^{-1}which is the characteristic peak for polysaccharide structure attributed to C-O stretching vibration. A characteristic peak of NaAlg appeared at 840 cm^{-1}which is attributed (Na-O).

The FTIR spectrum of the prepared copolymer, as observed in Fig.(7), shows bands at 3428, 2924 and 2854 cm^{-1}which are characteristic for stretching vibration of O-H, C-H, and CH_2, respectively. The characteristic stretching vibration bands at 1562 and 1033 cm^{-1} are attributed to NH_2 and alcoholic OH, respectively [30]. The band at 1459 $cm^{-1}$is for C-H bending of CH_3.The intensity of the stretching band of the carbonyl group C=O at 1750 cm^{-1}increased and shifted to 1738 cm^{-1}. The peak of NaAlg which appeared at 840 $cm^{-1}$was not obtained in the spectrum of the grafted copolymer. The FTIR spectrum confirmed that the radiation-induced chain degradation of NaAlg proceeds by the scission of the glycosidic bonds and the formation of unsaturated double bonds without a significant change in chemical structure[31].

CONCLUSION

The grafted copolymer was prepared by gamma radiation-induced copolymerization of NaAlg with AcA and MAcA in the presence of an MBA as a crosslinker. The optimum conditions for preparing the copolymer was fixed at 30 mass% of total monomers (20% AcA and 10% MAcA) and 0.4wt % sodium alginate at an irradiation dose of 15.0 kGy which displays a suitable swelling percentage using 0.03% of MBA as a crosslinker. The swelling percentage decreases with increasing irradiation dose from 15-30 kGy and MBA crosslinker concentration from 0.01-0.06, while the swelling percentage increases with increasing the pH solution from 1-13. It also increases with increasing Na Alg concentration till 0.2wt %, after which it decreases till 1.0 wt%.

The surface morphology of the prepared grafted copolymer shows a smooth surface and relatively homogeneous appearance. The Thermo-gravimetric analysis of the prepared grafted copolymer shows a good thermal stability suitable for all the domain of the practical application in which this polymer is used till near 400°C.

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