



Synthesis of acrylic acid onto potato starch using Diode Laser

Mohamed G. M. Sulaiman¹ and Ammar AL-Farga²

¹Chemistry Department, Faculty of Science, University of Jeddah, Jeddah,
Saudi Arabia

²Biochemistry Department, Faculty of Science, University of Jeddah,
Jeddah, Saudi Arabia

Corresponding author: Mohamed G. M. Sulaiman

Tel: +966550374575

E-mail address: *mgsulaiman@uj.edu.sa*

Abstract

Grafting of acrylic acid onto potato starch in aqueous medium initiated by diode laser has been studied under N₂ gas. The optimum conditions with respect to monomer concentration (acrylic acid AA), initiator concentration, graft copolymerization temperature, graft copolymerization time and exposure time of diode laser were studied in terms of percentage grafting efficiency (%GE) and percentage grafting yield (%GY). Potato starch-g-AA graft copolymer was characterized by FTIR, TGA for thermal stability, x-ray diffraction (XRD) for their crystallinity and scanning electron microscope (SEM) for surface morphology. The graft copolymer will be later used in drug delivery carrier to control cancer in brain and matrices for colon aiming medicine delivery systems. This study focused to new trends and latest developments in this area where diode laser was found to be efficient and clean method for synthesis Potato starch-g-AA.

Key words: Potato starch, Graft Efficiency, Diode Laser, Grafting Yield, Drug Delivery Carrier.

1. Introduction:

Starch is a polysaccharide and present mainly in the form of hydrocolloids. It is the most abundant form of carbohydrate present in nature and has the highest rate of biodegradability [1,2]. Starch can be obtained from different sources such as grains, wheat, rice and green plants. Starch is soluble in water and present in two forms namely amylose and amylopectin. Amylose is the linear form while amylopectin is the branched form of starch (Figure 1). Both forms of the starch differ in the biodegradability, elongation and strength. Starch can be used for grafting because of its low cost, easily available, biodegradable and environment friendly [3].

Starch is polymer having range of commercial applications, such as in superabsorbent [4], in adhesives [5], as removing organic dyes from aqueous systems [6] and as biodegradable thermoplastics in plastics industry [7]. Many vinyl monomers grafting the starch using this method [8,9] including grafting of potato starch by acrylic acid with $(\text{NH}_4)_2\text{S}_2\text{O}_8$ (APS) as an initiator [10].

Among the variety of initiating the vinyl monomer onto polysaccharides, C.A.N have the simple mechanism of electron transfer, and free radical formation [11]. As with cellulose, starch, chitin and chitosan the ceric ion a useful initiation for graft copolymerizing Gum Arabic, Gum Karaya and starch [12,13].

To impart desired properties onto polymers, by the use of high energy source (g-ray, e-beam), plasma, UV, and laser (excimer, Ar^+ laser), has been utilized through few years [14,15].

Applying the radiation in grafting enables the change of polymer wettability, adhesion, printability, metallization, antifog properties, antistatic properties, and biocompatibility [16]. Radiation-induced grafting did not leaving residue [17]. We can initiate graft copolymerization in emulsion and in solid state [18]. We can add new properties to the obtained graft copolymers [19].

Irradiation can be making out in air, inert atmosphere (e.g. N_2) or preferably under vacuum. These conditions include the addition of polymerization inhibitors such as Fe

and Cu salts, the use of good swelling agents (solvent), the selection of low dose rate [20].

If irradiation step is making out in air, the generated radicals shape peroxides and hydroperoxides, which initiate grafting upon connecting monomer units by thermal decomposition [21].

Laser light initiate grafting of monomers has attracted attention, therefore capability of laser to be adjusted to a specific wavelength, therefore exciting a particular band [22,23].

Decomposition of cyclohexene -1, 4-cyclohexadiene and hexahydro-1, 3, 5-trinitro-1, 3, 5 -triazine molecules excited via a multi photon process by employ of CO₂ transverse electrical discharge in gas and atmospheric pressure (TEA CO₂) laser has been present by Zhao and coworkers [24,25]. Exterior alteration over etching in the being of air by CO₂ -pulsed laser has also done [26]. The capability of CO₂ - pulsed laser to graft many monomers on the surface of ethylene-propylene rubber to improved water and biocompatibility has been explained [27,28]. Ethylene-propylene rubber (EPR) has been surface grafted with acrylamide (AAm) and 2-hydroxy ethyle methacrylate (HEMA) using a CO₂ - pulsed laser [29].

Much work has been doing on the grafting of acrylonitrile [30,31,32], acrylic acid [33] and acrylamide [34,35] onto starch and its derivatives. Grafting of acrylonitrile onto gaur gum [36,37], cellulose [38,39] and chitosan [36]. Meanwhile, several works do preparation of super absorbing polymers via alkaline hydrolysis of polyacrylonitrile (PAN)-grafted polysaccharides [31,37,38,40,41,42].

Recently a laser light used as initiator for grafting many monomers such as 3,3-dimethyle acrylic acid grafted on GA [43]. Gum Karaya -g-acrylamide [44], Graft polyacrylamide onto GA [45]. 3,3-dimethyle acrylic acid grafting in Gum Karaya [46], Gum Arabic-g- Acrylic acid [47], and Synthesis of Gum Arabic-g-polyaniline using

diode laser this study focused to new trends and latest developments in this area where diode laser was found to be efficient and, clean method for synthesis GA-g-PANI [48].

Nevertheless, as far as our information is concerned, until now, there is no literature concerning any research on the synthesis of potato starch -g- acrylic acid using laser diode anywhere else in the world.

2. Experimental:

Materials:

Potato starch was obtained from Sigma Aldrich and acrylic acid was obtained from Merk. Distilled water was used as a solvent. Nitric Acid (Molar Solution), Ethanol Absolute Assay > 99.8% supplied from England, and ceric ammonium nitrate C.A.N (Aldrich).

1. Diode laser with wavelength of 532 nm and Power of 200 mW, supplied from (USA), continuous wave (CW) output.

2. Fourier transform infrared spectrometer (FT-IR), model *Perkin Elmer 2000 FT-IR* system supplied from (Perkin Elmer, Norwalk, CT), using the KBr disk method (2 mg sample in 200 mg KBr) and then pressed into tablets. The scanning range was 500 to 4000 cm^{-1} and the resolution was 1 cm^{-1} .

3. X-ray Diffraction was obtained by using Xe filled counteract solid state, system attached with liquid nitrogen cooled detector, model *Bruker D 8 Advance* (Germany), equipped with a θ - θ goniometer under the following operation conditions: 40 KV and 40 mA with CuK α -radiation at λ 1.54056Å°. The relative intensity was recorded in the scattering range (2θ) of 4 – 60°.

4. Thermogravimetric analysis system (TGA) was recorded on a Rigaku Thermoflex, PTC-10A, Rigaku Corporation, Japan with 10 °C per min heating rate and Alumina as reference material, with the range of temperature from 10 to 700°C.

5. Scanning Electron Microscope (SEM), supplied from JEOL (Japan) model 840 A^o with an acceleration voltage of 1.0 kV, Samples were freeze-dried and by making a film of desirable size and coated with gold powder prior to SEM. Images were captured using an 11.20 mm Ricoh Camera.

Methods:

(1)- Graft Copolymerization with (CAN):

Weight 0.5 gram of potato starch and added 75 mL of water, stirred magnetically under nitrogen for five minutes, added required amount of (CAN) in molar nitric acid stirring for fifteen minutes to make possible consistence of ion one pair sites on the chain of starch, followed by addition drop wise of acrylic acid. Complete the volume to 100 mL using distilled water. The grafting executed at 30° C for 3 hours. The solution was cooled, clean with water ethanol many times to extract homopolymer and monomer did not react. The product was dried at 38°C to a constant weight.

(2) - Graft Copolymerization by Laser:

Weight 0.5 gram of potato starch and added water seventy five ml, stirred magnetically five minutes in nitrogen. Diode laser was used, as initiator, to irradiate the sample. The acrylic acid (monomer), complete the volume to 100 mL using water. The grafting executed at 30° C for 3 hours. The solution was cooled, clean with water ethanol many times to extract homopolymer and monomer did not react. The final product was dried at 38°C to a fixed weight, and then proportion of (%GE) and (%GY) studied as follow [49,50]:

$$(\%GE) = 100 (W_2 - W_1) / W_1 \quad (1)$$

$$(\%GY) = 100 (W_2 - W_1) / W_3 \quad (2)$$

Where W_1 , W_2 , and W_3 denote weights of the potato starch, graft copolymer and monomer, respectively.

3. Results and Discussion

Grafting of AA onto starch initiated by CAN was carried out depending upon different concentrations of CAN at different temperatures and various times to optimize the reaction conditions. The optimum conditions were starch (0.5 g/L), AA (0.142 g/L), and CAN (0.91×10^{-3} M) at 30 °C in three hours. The percentage of graft efficiency and graft yield at the optimum conditions were 26 % and 76 %, respectively (figure 1). While the optimum conditions using laser irradiation (532 nm) were starch (0.5 g/L), AA (0.142 g/L), reaction temperature 30 °C, and 60 minutes exposure time. With percentage of graft efficiency and percentage of graft yield 36 % and 90 %, respectively (figure 2).

According to the grafting of AA onto starch using CAN and diode laser irradiation results which present that the grafting with diode laser irradiation is more effective than that with CAN.

3.1. Characterization of potato starch -g- AA

3.1.1. Gravimetric Estimation

The noticeable weight difference between potato starch -g- AA and potato starch gives a clear evidence of grafting of AA onto potato starch. This weight difference forms the basis for the determination of grafting efficiency (%GE).

3.1.2. FTIR analysis

Figure (5) shows FTIR spectra of potato starch, acrylic acid, and potato starch-g-AA. In FTIR spectrum of potato starch a broad absorption band at 3395 cm^{-1} for O-H stretching vibrations and a smaller absorption band at 2925 cm^{-1} attributed to C-H stretching

vibration are observed. Wave numbers at 1153, 1078 and 1020 cm^{-1} describe C-O-C stretching (triplet for starch) and a band at 1638 cm^{-1} corresponds to water molecule [25].

More interesting are the peaks at ca 1700 cm^{-1} , these are present both in pure AA and in the grafted potato starch but not in the potato starch. They can be attributed to carbonyl groups (C=O). The mere fact that, even after the severe separation procedure a distinct peak from carbonyl groups appears in the product means that there is AA present in it. This is proof that the acrylic acid is chemically grafted onto the potato starch backbones.

3.1.3. TGA analysis

The thermal behavior of pure and grafted starch is very clearly exhibited by the thermograms and derivatograms (Fig.4). Though both pure and grafted potato starch led to a two-stage weight loss, the onset temperature of decomposition. Pure starch shows a characteristic three-step thermogram, where in the major weight loss (75.5%) occurs in the second step within the temperature range of 233-368°C. The third stage of decomposition is rather slow and results in about 11% weight loss up to 495°C.

In case of grafted potato starch, the onset temperature of decomposition for the second step was as low as 133°C as against 233°C for that of pure potato starch. It is evident from table (1) that the grafted potato starch is thermally stable than the potato starch

3.1.4 X-ray Diffraction (XRD)

The X-ray diffraction pattern of potato starch and potato starch-g-AA is shown in Figure (5). Potato starch is known to be semi crystalline in nature due to the amylopectin fraction that exists into it. The area of crystallinity shows about 20 to 25% crystallinity of the total volume of potato starch granules [31]. Upon grafting of potato starch with AA polymer the number of counts of copolymer dropped too much from 1000 count for potato starch to 200 counts for potato starch-g-AA copolymer. This large reduction in crystallinity suggest that the grafting of AA polymer cause destruction of crystalline region and thus suggest that along with amorphous region, the crystalline region of potato starch is also involved in grafting [32].

3.1.5 SEM photography

From SEM photographs the morphology of potato starch, and potato starch-g- AA can be determined. The scanning electron micrograph of potato starch shows a granular structure (Fig 6a). The grafted polymer (potato starch-g- AA), showed different morphology, which it's a porous structure can be seen in (Fig 6b). Such hollow structures may result from the agglomeration of smaller particles.

4. Conclusions

Graft copolymer of potato starch -g- AA was successfully synthesized by graft copolymerization using the initiator diode laser. The graft copolymer was characterized by FTIR and XRD, which elucidated the structure changes in comparison with pure potato starch. The SEM micrograph of grafted potato starch showed a porous structure providing better adsorption sites. TGA analysis revealed that graft copolymer had more thermal stability. The results of grafting yield and grafting efficiency from the graph confirm that graft copolymerization has been successively achieved.

Acknowledgement

This work was funded by the Deanship of Scientific Research (DSR), University of Jeddah, Jeddah, Saudi Arabia, under grant No. (UJ-20-024-DR). The authors, therefore, acknowledge with thanks University of Jeddah DSR technical and financial support.

References:

1. Jyothi A.(2010) Starch graft copolymers: Novel applications in industry. *Compo Inter*, 17: 165-174.
2. Zou W.(2012) Effects of amylose/amylopectin ratio on starch-based superabsorbent polymers. *Carbohydr Polym*, 87: 1583-1588.
3. Biswas A.(2006) Ionic liquids as solvents for biopolymers: Acylation of starch and zein protein. *Carbohydr Polym*, 66: 546-550.
4. Teli MD, Waghmare NG. (2010). Synthesis of superabsorbents from Amaranthus starch. *Carbohydr. Polym*; 50(4):695-699.
5. Wang Z, Li Z, Gu Z, Hong Y, Cheng L. (2012) Preparation, characterization and properties of starch based wood adhesive *Carbohydr. Polym*; 88(2):699-706.
6. Pathania D, Sharma R, Kalia S.(2012) Graft copolymerization of acrylic acid onto gelatinized potato starch for removal of metal ions and organic dyes from aqueous system. *Adv. Mat. Letter*; 3(2):259-264.
7. Fang JM, Fowler PA, Tomkinson J, Hill CAS. (2002) An investigation of the use of recovered vegetable oil for the preparation of starch thermoplastics. *Carbohydr. Polym*; 50(4):429-434.
8. Athawale VD, Rathi SC. (1997) Effect of Chain Length of the Alkyl Group of Alkyl Methacrylates on Graft Polymerization onto Starch Using Ceric Ammonium Nitrate as Initiator *Eur. Polym J.*; 33(7):1067-107.
9. Sharma BR, Kumar V, Soni PL.(2003) Graft copolymerization of acrylonitrile onto Cassia tora gum with ceric ammonium nitrate–nitric acid as a redox initiator. *J.Appl. Polym. Sci.*; 90(1):129-13.
10. Lele V. (2015) Grafting parameters of copolymers of insoluble potato starch with acrylic acid. *Scholars World*; 3(3):22-28.
11. Fernandez M.J., Casinos I., Guzman G.M.,(1990), on the graft copolymerization. Effect of the way of addition of reactants in the graft copolymerization of a vinyl acetate

methyl acrylate mixture onto cellulose, *J. Polym. Sci., Part A: Polym. Chem.*, 28, 2275-2292.

12. Pourjavadi A., Mahdavinia G.R., Zohuriaan-Mehr M.J.,(2001), Acrylonitrile grafting onto chitosan, *Proceedings of the 5th Austrian Polymer Meeting*, Leoben, Austria, p.77, 12-14.

13. Mahdavinia G.R., Pourjavadi A., Hosseinzadeh H., Zohuriaan M.J.,(2004), Modified chitosan .4.Superabsorbent Hydrogels from poly (acrylamide-co-acrylic acid) grafted chitosan with salt- and pH-responsiveness properties, *Eur.Polym. J.*, 40, 1399-1407.

14. S. H. Choi and Y. C. Nho,(2000), *Radiat. Phys. Chem.*, 57, 187.

15. F. Severini, M. Pegoraro, L. Yuan, G. Ricca, and N. Fanti,(1999), *Polymer*, 40, 7059.

16. Betz N, Begue J, Goncalves M, Gionnet K, Deleris G, (2003), Le Moel A. Functionalisation of PAA radiation grafted PVDF. *Nucl Instrum Meth Phys Res*,41, 208 - 434.

17. Abdel-Bary EM, El-Nesr EM.,(1997), Methods, characterization, and application of grafting. In: Cheremisinoff NP, editor. *Handbook of engineering polymeric materials*. New York: Marcel Dekker; p. 501.

18. Chapiro A.,(1977), Radiation induced grafting. *Int J Radiat Phys Chem* 9,55–67.

19. Guilmeau I, Esnouf S, Betz N, Le Moel A.,(1997), Kinetics and Characterization of radiation-induced grafting of styrene on fluoropolymers. *Nucl Instrum Meth Phys Res*, 5, 131-270.

20. Nasef M, Saidi H, Nor H.,(1999), Radiation-induced graft copolymerization for preparation of cation exchange membranes: a review. *Nucl Sci J Malaysia*,43,17-27.

21. Aydinli B, Tincer T.,(2001), Radiation grafting of various water soluble monomers on ultra-high molecular weight polyethylene powder. I. Grafting conditions and grafting yield. *Radiat Phys Chem*,43, 60 -237.

22. Kesling W. Koine! D., and Schollmcyer F..S., (1990), *Angew. Mukroat& Chem.*, 182, 177.
23. Hoyle C .E ., Chang C .H. and Trapp M .A .,(1989), *Macromolecules*, 22, 3607-3610.
24. Zhau X ., Continetti R .E ., Ynkuyama A . . Ilintsa E .J . and I .ec Y.T., *J.*,(1989), *Chem . Phys.*, 91 ; 4118.
25. Zhao X ., Hinsta FJ . and Lee Y .T.,(1988), *J. Chem. Phys.*, 88, 811.
26. Brannon J .H . . Lankari J .R .,(1986), *Appl . l'hr• .+ . Lett. .* 48, 1226.
27. Mirzadeh H ., Kathah A .A ., Burford R .P.,(1993), *Rad. Phys. Chem.*, 41, 507-519.
28. Mirzadeh l.l., Khorasani M.'l., Katbab A.A., Ilurford R .Y.,Sohcili Z .,(1994), Cinlestani A. and [ioliaei B . . *Clinical Materials*, 16, 177-187.
29. Mirzadeh H, Katbab AA, Khorasani MT, Burford RP.,(1994) Laser induced surface grafting of HEMA and NVP onto ethylene-propylene rubber as biocompatible material. *Angew Makromol Chem* 18, 2340.
30. M. J. Zohuriaan- Mahr, A. Pourjavadi, (2003), New polysaccharide-g-polyacrylonitrile copolymers: Synthesis and thermal characterize-ation. *Polm. Adv. Technol.*14,508-516.
31. L. A. Gugliemelli, M. O. Weaver, C. R. Russell, C. E. Rist, (1969), Base-hydrolyzed starch- polyacrylonitrile (S-PAN) graft copolymer. S-PAN 1:1 PAN M.W. 794,000.J. *Appl. Polym. Sci.* 13, 2007-2017.
32. J. Gao, J. Yu. W. Wang, L. Chang, R. Tain, (1998), Graft copolymer-ization of starch-AN initiated by potassium permanganate. . *J. Appl. Polym. Sci.* 68, 1965-1972.
33. V.D. Athawale, V. Lele, (1998), Graft copolymerization onto starch. II Grafting of acrylic acid and preparation of its hydrogels. *Carbohyr. Polym.* 35, 21-27.

34. H. El-Hamshary, S. Al-Sigeny, M. M. Ali, (2006), Synthesis and biological study of some amino acid functionalized starch-g- polyacrylamide. *Carbohydr. Polym.* 64, 282-286.
35. Y. Cao, X. Qing. J. Sun, F. Zhou, S. Lin, (2002), Graft copolymerization of acrylamide onto carboxymethyl starch. *Eur.Polym. J.* 38, 1921-1924.
36. J. H. Trivedi, K. Kalia, NK. Patel, H. C. Trivedi, (2005), Ceric induced grafting of acrylonitrile onto sodium salt of partially carboxymethylated guar gum. *Carbohydr. Polym.* 60,117-125.
37. R. T. Thimma, N. S. Tammishetti, (2003), Synthesis and characterization of guar gum-g- polyacrylonitrile .*Polym. Adv. Technol.* 14, 663-668.
38. S. Farag, E. I. Al-faleq, (2002), Preparation and characterization of delignified cellulose polyacrylonitrile-g-Copolymer. *Carbohydr. Polym.* 48, 1-5.
39. E. Bianchi, E. Marsano, L. Ricco, S. Russo, (1998), Free radical grafting onto cellulose in homogeneous conditions 1-modified cellulose -acrylonitrile system, *Carbohydr. Polym.* 36,313-318.
40. G. R. Mahdavinia, M. J. Zohuriaan- Mahr, A.Pourjavadi, (2004), Modified chitosan III. Superabsorbency,salt-and PH-sensitivity of smart ampholytic hydrogels fromchitosan -g-PAN, *Polym. Adv. Technol* 15,173-180.
41. D. W. Lim, H. S. Whang, K. J. Yoon, S. W. Ko, (2001), Synthesis and absorbency of a superabsorbent from sodium starch sulfate-g- polyacrylonitrile. *J. Appl. Polym. Sci.* 79, 1423-1430.
42. Y. Sugahara, T. Ohta, (2001), Synthesis of starch-g-polyacrylonitrile hydrolyzate and its characterization. *J. Appl. Polym. Sci.* 82, 1437-1443.
43. Nafie, A. H.Elfatih, Al Sayed, & G. M. S.Mohamed, *International Research*

Publications:Materials, Methods & Technologies,2010, 5; 1-14.

44. Nafie, A. H.Elfatih, Al Sayed, & G. M. S.Mohamed, *Chemical Physics: Elixir Chem. Phys.* 2011,33; 2227-2230.
45. Nafie, A. H.Elfatih, Al Sayed, & G. M. S.Mohamed, *Journal of Physical Science* 2012,23,2; 43–53.
46. Mohamed, S.Mohamed , A,Adam, Essam & Elb. *International Journal of Recent Scientific Research* 2015, 6; 2428-2433.
47. Mohamed G. M. Sulaiman, *International Journal of Science and Technology*, 2019, 5(3), 86-97.
48. Sulaiman MGM, Al-Farga A. Synthesis of Gum Arabic-g-polyaniline using diode laser. *Int J Biol Macromol.* 2020 Oct 15;161:848-853. doi: 10.1016/j.ijbiomac.2020.06.111. Epub 2020 Jun 15. PMID: 32553975
49. R.K. Sharma, Lalita, G.S. Chauhan, R. Verma, Graft copolymers of acrylonitrile onto dextrin for use in separation technologies, *Int. J. Polym. Mater.* 59 (2010) 263–285.
50. T.K. Giri, M. Pradhan, D.K. Tripathi, Synthesis of graft copolymer of kappacarrageenan using microwave energy and studies of swelling capacity, flocculation properties, and preliminary acute toxicity, *Turk. J. Chem.* 40 (2016) 283–295.

Table 1: Thermogravimetric information with heat at 10 °C/min under nitrogen for potato starch and potato starch - g-acrylic acid.

Sample	Stages number	Temperature (°C)	% Loss of Weight
Potato starch	1	37 – 100	11.8
	2	233 – 417	75.5
	3	417 – 495	10.6
potato starch-g-acrylic acid	1	35 – 133	10.5
	2	133 – 303	43.6
	3	333 - 352	45.7

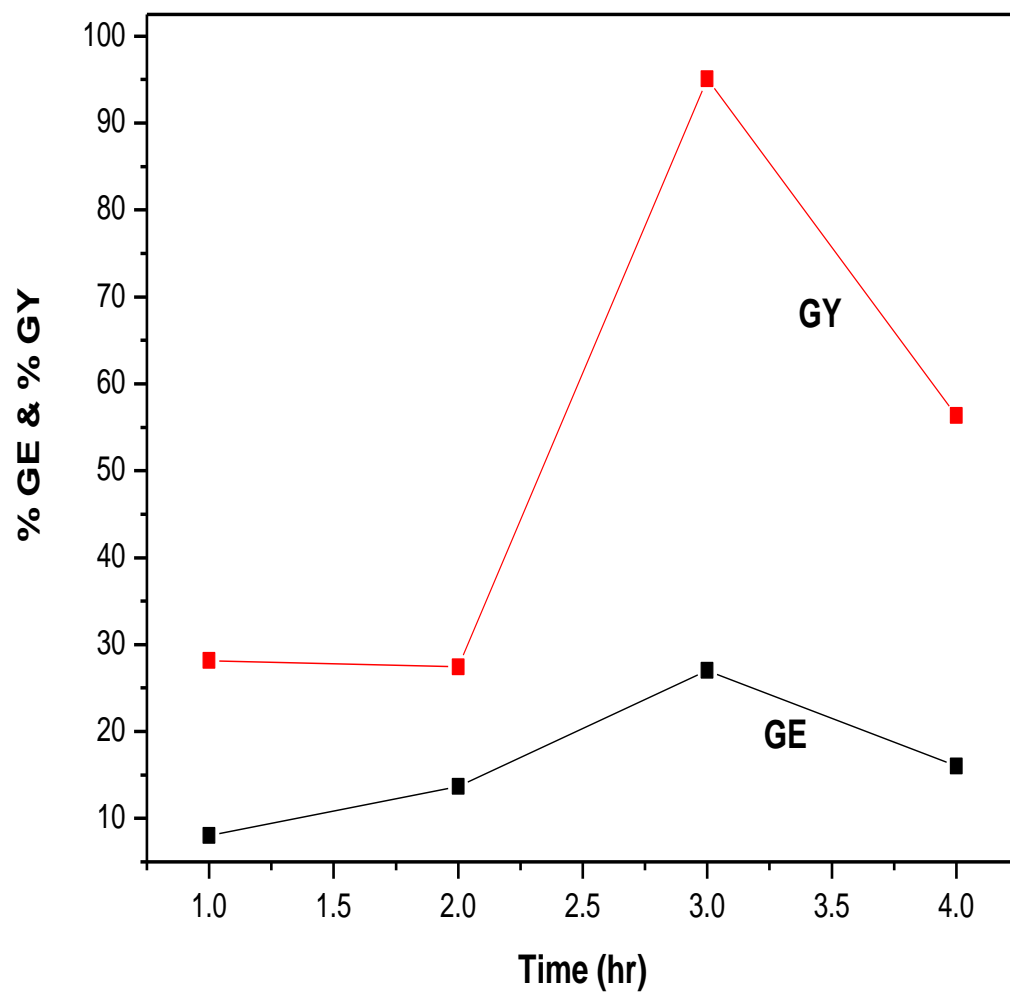


Figure 1: Effecting reaction time of grafted copolymer, acrylic acid, and CAN.

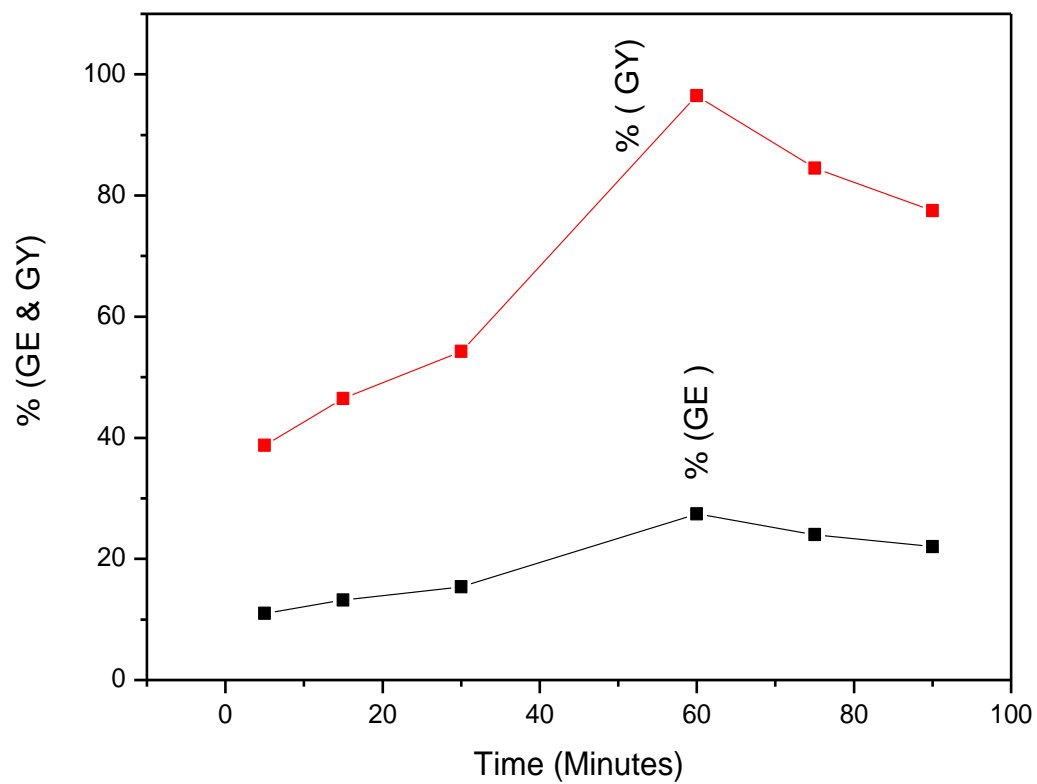


Figure 2: Effect exposure time of laser on (%GE) and (%GY) of starch -g- AA

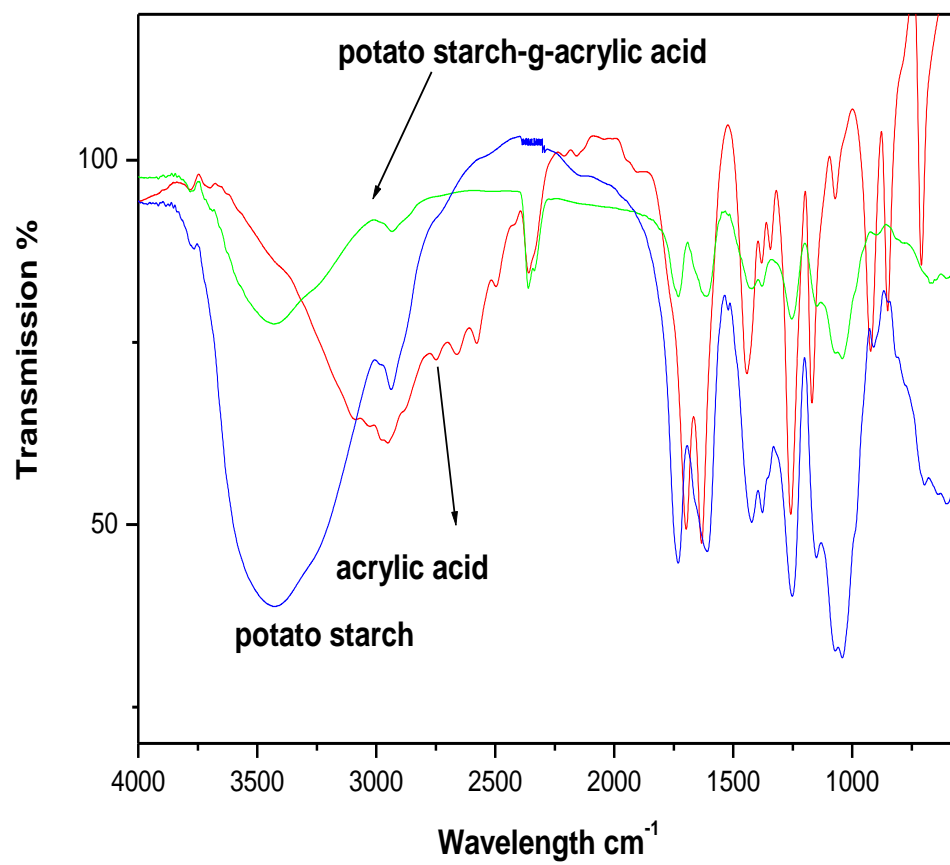


Figure 3: FTIR spectra of potato starch, potato starch –g- acrylic acid, and of acrylic acid.

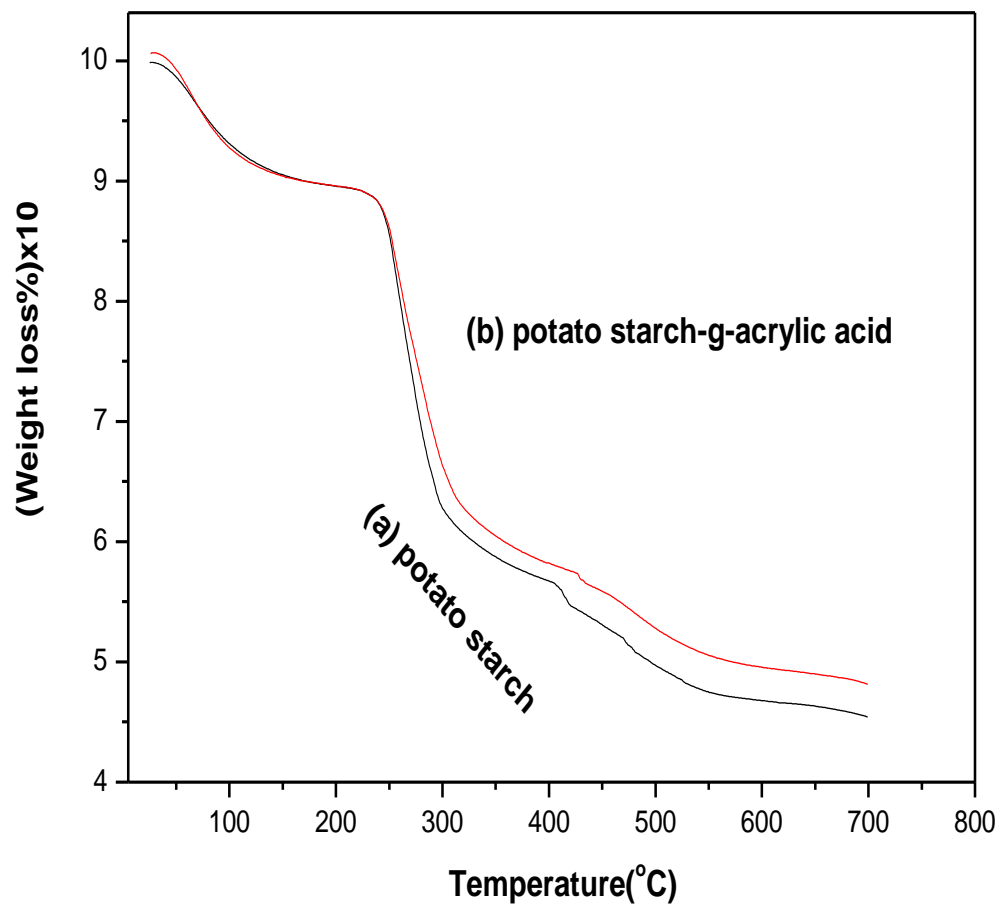


Figure 4: Thermograms of potato starch (a), and potato starch-g- acrylic acid

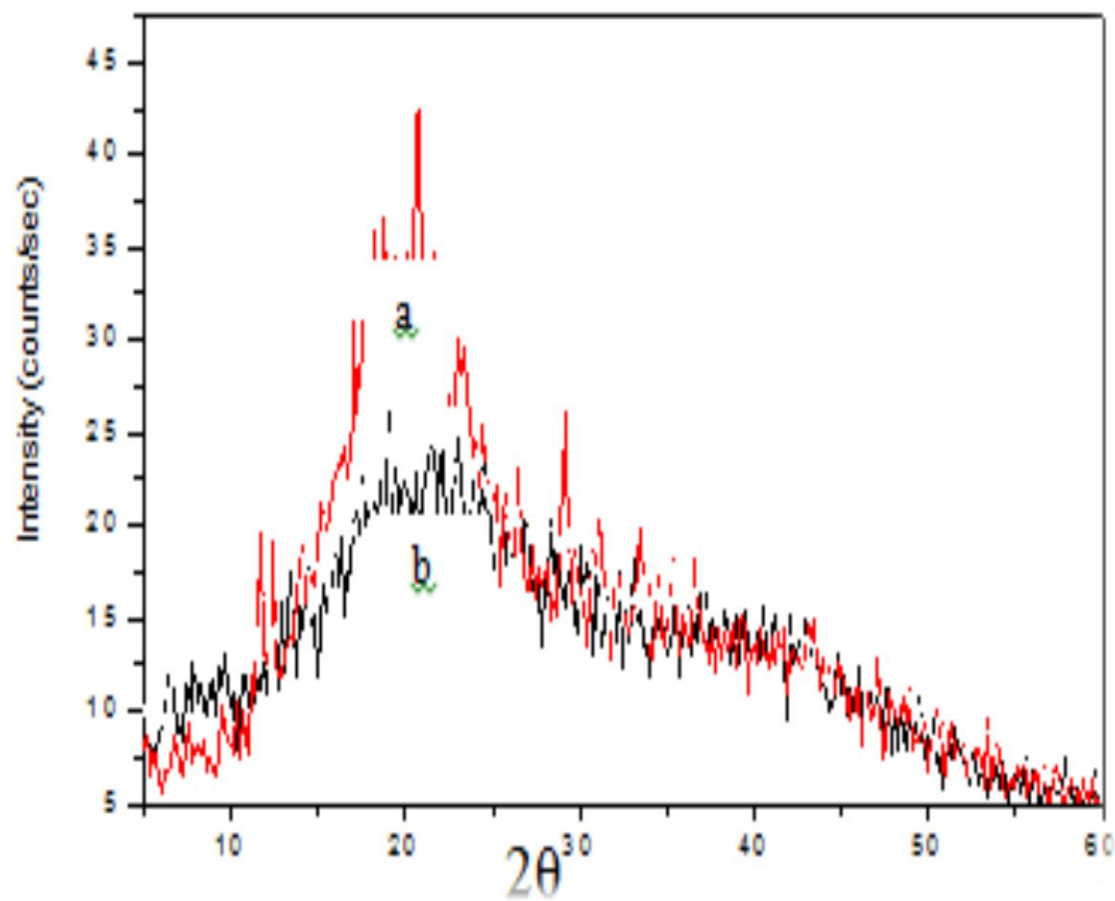


Figure5: X-ray diffraction pattern for: (a) potato starch; (b) potato starch-g-AA.

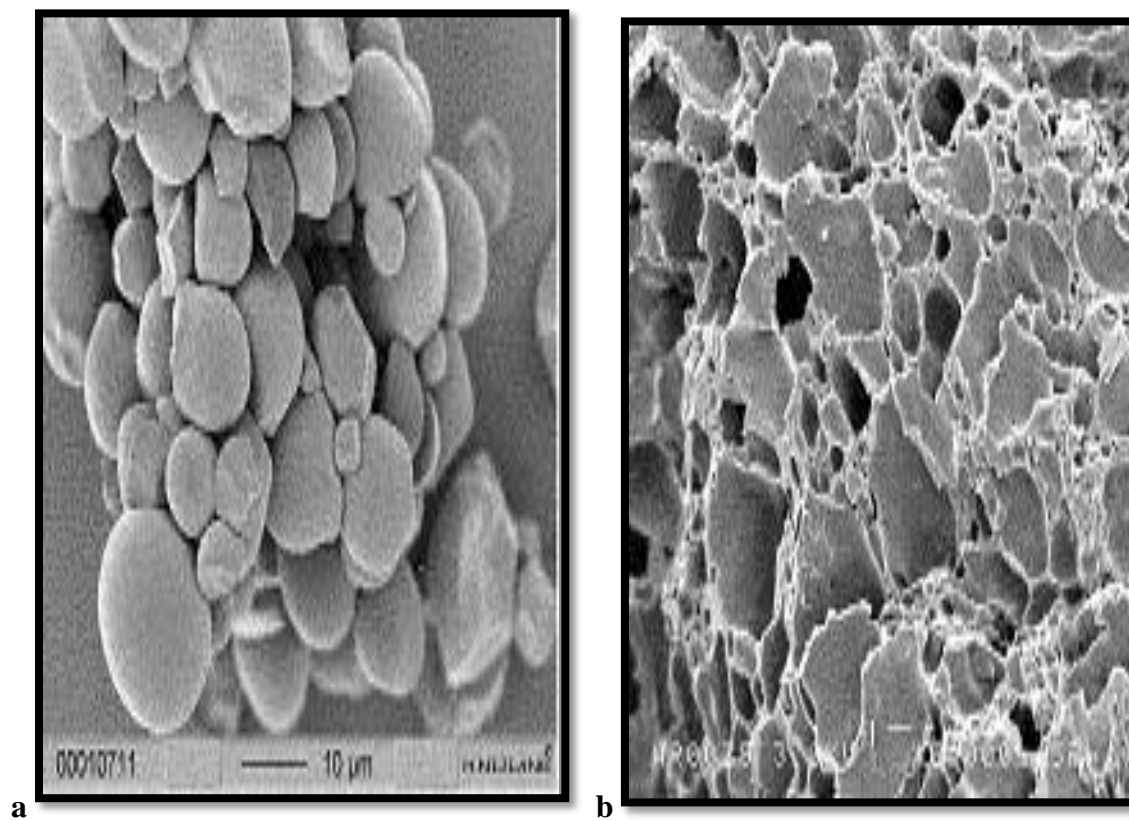


Figure 6: SEM photographs of: (a) Potato starch (b) potato starch-g- AA