A Study on Effect of Different Reaction Conditions on Grafting of Psyllium and Acrylic Acid-Based Hydrogels

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ABSTRACT: In this study, Psyllium and acrylic acid based polymeric networks were synthesized under different reaction conditions such as in-air, in-vacuum, and under the influence of γ-radiations using potassium persulphate (KPS)-hexamethylene tetramine (HMTA) as an initiator-crosslinker system. Initially, optimization of varied reaction parameters was performed under all the different reaction conditions. The synthesized networks were then characterized using FTIR spectroscopy, SEM, TGA/DTA, and XRD techniques. It has been found that the percent grafting varies with varying reaction conditions with maximum grafting (138 ± 1.15%) reported in case of synthesis carried-out in-vacuum followed by the synthesis in-air (125 ± 1.00%) and then in case of synthesis under the influence of γ-radiations (124 ± 1.15%). © 2011 Wiley Periodicals, Inc. J Appl Polym Sci 123: 1874–1883, 2012

Key words: grafting; hydrogels; polymeric network; psyllium; acrylic acid

INTRODUCTION

Functionalization of natural polysaccharide using different monomers for use in broadened areas has been the major focus of scientists these days. Numerous studies revealed the scientific importance of this research field for mankind. Graft copolymerization of acrylamide on cotton fibers and fabrics was studied in a limited aqueous system using potassium persulphate as an initiator. Grafting parameters under different sets of condition were determined and the mechanism of graft copolymer was discussed.[1] Now a days more emphasis is given to biodegradable polymers such as polysaccharides and proteins, which have been extensively used and investigated fir industrial applications.[2,3] Various natural polysaccharides such as Starch,[4] Guar gum,[5] cellulose,[2] Xanthan gum,[3] κ-Carrageenan,[6] chitosan,[7,8] and Psyllium[9–11] have been modified for their wide applications in variety of areas like waste water treatment,[12] biomedicine,[13] and food industry.[14]

Pande et al.[15] studied the functionalization of poly(vinyl chloride) through irradiation in air with γ-rays. In a study, polyacrylamide-grafted-guar gum was utilized for the controlled release of diltiazen hydrochloride, in the form of tablet.[16] Potassium persulphate/ascorbic acid were used as initiators in gravimetrically grafting of methylmethacrylate onto *Cyanaposis tetragonolobus* seed galactomannan.[17] Singh et al.[18] studied microwave assisted synthesis of guar-g-polyacrylamide and reported that the grafting yields are comparable to that obtained through KPS/ascorbic acid initiated thermal polymerization. Preparation of polyaniline film from oxidative polymerization of aniline using potassium persulphate and its deposition has been studied by Ayad and Shenasmin.[19] Radical induced polymerization technique has been used to crosslink acrylamide with *N, N′*-methylene bisacrylamide.[20,21] Abdel-Hafiz[22] studied the graft copolymerization of methacrylic acid onto loomstate cotton fabric under different reaction conditions using $KMnO_4$/ thiourea dioxide system as an initiator. El-Naggar et al.[23] used preirradiation technique for graft copolymerizing acrylamide onto Nylon-66. Graft copolymer from poly(acrylamide) and poly(ethylene oxide-*co*-propylene oxide) was synthesized for the investigation of rheological behavior of the grafted product.[24] Kaith and Kumar[9–11] synthesized the graft copolymers of psyllium with different vinyl monomers and studied the absorption of water from different petroleum fraction-water emulsions. Mirzadeh et al.[25] grafted acrylamide onto ethylene-propylene powder using CO_2-pulsed lased induced surface grafting technique in presence of benzophenone and azobis-isobutyronitrile. The synthesized product was characterized with FTIR and SEM.

Since the authors have carried-out the synthesis of psyllium based hydrogels with different vinyl monomers under different reaction conditions like in air, under vacuum and under the influence of γ-radiations, therefore, a comparison of the impact of different reaction conditions on physical and chemical properties on psyllium-based hydrogels has been exhibited in the present communication.

EXPERIMENTAL

Materials

Plantago Psyllium (Sidhpur Sat-Isabgol Factory), acrylic acid (Merck-Schuchardt), potassium per sulfate (S. D. Fine) and hexamethylene tetramine (S. D. Fine) were used as received. Double distilled water was used as solvent for the synthesis of graft copolymer.

FTIR spectroscopy

PERKIN ELMER RXI Spectrophotometer was used for taking FTIR spectra of the samples using KBr pellets.

Scanning electron microscopy

JEOL STEROSCAN 150 MICROSCOPE was used for capturing SEMs of the samples.

Thermogravimetric analysis/differential thermal analysis

Thermogravimetric analysis/differential thermal analysis (TGA/DTA) studies were carried-out on Linseis, L-81 11 thermal analyzer in air at a heating rate of 10°C/min.

X-ray diffraction studies

X-ray diffractometer (BRUKER AXS D8 ADVANCE) was used to carry-out X-ray diffraction studies. The studies were performed under ambient conditions on Bruker-D_8 advance model using Cu Kα (1.5418 °A) radiation, Ni-filter and scintillation counter as detector at 40 KV and 40 mA on rotation between 0.5° or 1.0 mm of divergent and antiscattering slit. Psyllium and Psy-cl-poly(AA) were converted to small particle size through crushing in the mortar pestel and homogeneous sample of each polymer was subjected for X-ray diffractometry. The sample holder was made of PMMA polymer and consisted of round central cavity. Outer diameter of the holder was 50 mm, central cavity had diameter of 25 mm which retained the sample of height 1 mm and the holder height was 8.5 mm. The holder was then held in vertical position and the sample was tapped gently. A glass slide was clipped up to the top face of the sample holder first, so as to form a wall of the sample in symmetry to the holder walls. This procedure was repeated until the cavity was filled. Finally, the glass slide was carefully removed without disturbing the sample surface. Powder outside the central cavity was removed with tissue paper. Corrundum was the reference to calibrate the instrument.

The randomly oriented powdered sample with a uniform surface was exposed to X-rays from all possible planes of the sample and then measuring the scattering angle of the diffracted X-rays with respect to the angle of the incident beam. The continuous scans were taken and relative intensity was obtained. Crystalline index (C.I.), which measures the orientation of the crystals in a polysaccharide to the polysaccharide axis, was determined by using the wide angle X-ray diffraction counts at 2θ angle close to 21.297 and 34.744°. The counter reading at peak intensity of 21.297° is said to represent the crystalline material and the peak intensities at 34.744° corresponds to the amorphous material in Psyllium.[26] Percentage crystallinity (%Cr)[27] and the crystalline index[28] were calculated as follows:

$$\%Cr = \frac{I_{21.297}}{I_{21.297} + I_{34.744}} \times 100$$

$$C.I. = \frac{I_{21.297} - I_{34.744}}{I_{21.297}}$$

where $I_{21.297}$ and $I_{34.744}$ are the crystalline and amorphous intensities at 2θ scale close to 21.297 and 34.744°, respectively.

Synthesis

Synthesis of different crosslinked graft copolymers of Psyllium and acrylic acid was carried-out under three different reaction conditions: in-air (IA), in-vacuum (IV) and under the influence of γ-radiations (UR) using Co-60 as the source of radiation.

Psyllium (1.0 g) was taken in a flask and to it a known amount of double distilled water was added. To the reaction mixture a known amount of monomer was added and this was followed by the addition of an initiator and crosslinker dissolved previously in minimum amount of the water. Mixture was made uniform by thorough stirring. The reaction was carried-out under different reaction conditions such as in-air, in-vacuum and under the influence of γ-radiations. After completion of reaction, initially hot water was used for the removal of homopolymer, however, subsequent removal of homopolymer was done with soxhlet

TABLE I
Optimum Percent Grafting and Percent Swelling During Synthesis of Psy-cl-poly(AA) Under Different Reaction Conditions

Sample		M	±SD	±SE
Psy-cl-poly(AA)-IA	P_g	125.00	1.00	1.73
	P_s	3200.0	20.81	36.05
Psy-cl-poly(AA)-IV	P_g	138.0	1.15	2.00
	P_s	4380.0	20.81	36.05
Psy-cl-poly(AA)-UR	P_g	124.0	1.15	2.00
	P_s	10578.0	19.55	33.86

Where, No. of samples used in each case = 03; M, mean; ±SE, standard error of mean; ±SD, standard deviation.

refluxing for 24 h in 80% methanol. The synthesized polymers were dried to constant weight in hot air oven at 50°C. Optimization of different reaction parameters like reaction temperature, time, amount of double distilled water, pH, and initiator concentration was carried-out as a function of percentage grafting (P_g) following the standard method.[29] Whereas, optimization of monomer concentration and crosslinker concentration was carried-out as a function of percentage swelling (P_s) using the standard method.[30]

The replications carried-out for the reproducibility of the results were in triplicates and the statistical analysis of the results obtained was performed using Statistical Package for Social Science (SPSS) version 10. Statistical results of the optimum percent grafting and percent swelling are depicted in Table I.

RESULTS AND DISCUSSION

Mucilage forming fraction of psyllium i.e., arabinoxylan having xylopyranose straight chain with arabinofuranose branches at two or three positions acts as the active site for the graft copolymerization with the help of its hydroxyl groups. In case of reactions performed in-air and in-vacuum, mechanism for graft copolymerization of the monomer onto Psyllium can be presented through the following mechanism[31]:

Initiation

$$^-O_3S - O - O - SO_3^- \longrightarrow 2\,SO_4^{-*} \quad (1)$$

$$SO_4^{-*} + H_2O \longrightarrow HSO_4^- + {^*}OH \quad (2)$$

$$Psy - OH + SO_4^{-*} \longrightarrow Psy - O^* + HSO_4^- \quad (3)$$

$$Psy - OH + {^*}OH \longrightarrow Psy - O^* + H_2O \quad (4)$$

$$M + OH \longrightarrow {^*}M - OH \quad (5)$$

$$M + SO_4^{-*} \longrightarrow {^*}M - SO_4^- \quad (6)$$

Propagation

$$Psy - OH + {^*}M - OH \longrightarrow Psy - O - M^* + H_2O \quad (7)$$

$$Psy - O - M^* + nM \longrightarrow Psy - O - (M)_n - M^* \quad (8)$$

$$Psy - O^* + nM \longrightarrow Psy - O - (M)_{n-1}M^* \quad (9)$$

$${^*}M - OH + nM \longrightarrow HO - (M)_n M^* \quad (10)$$

Termination

$$Psy - O - (M)_n - M^* + M^* - (M)_n - O - Psy \longrightarrow$$
$$Psy - O - (M)_n - M_2 - (M)_n - O - Psy$$
$$\text{Graft co} - \text{polymer} \quad (11)$$

$$Psy - O - (M)_{n-1}M^* + M^* - (M)_{n-1} - O - Psy \longrightarrow$$
$$Psy - O - (M)_{n-1}M_2 - (M)_{n-1}O - Psy$$
$$\text{Graft co} - \text{polymer} \quad (12)$$

$$Psy - O - (M)_n M^* + {^*}OH \longrightarrow Psy - O - (M)_{n+1}OH \quad (13)$$

$$HO - (M)_n - M^* + {^*}M - (M)_n - OH \longrightarrow HO - (M)_n$$
$$- M_2 - (M)_n - OH\,\text{Homopolymer} \quad (14)$$
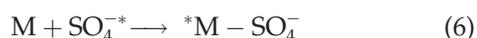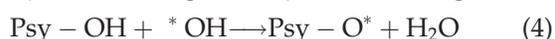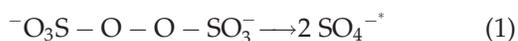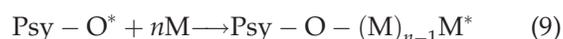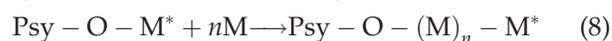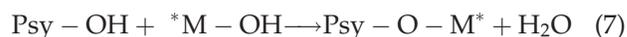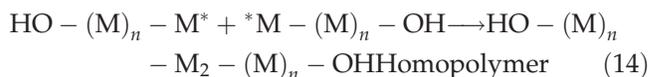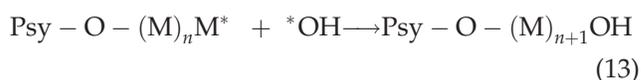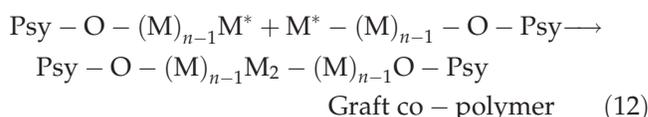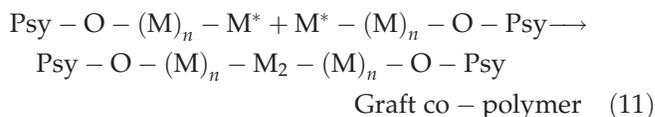
where M* = monomer free radical; Psy-O* = backbone free radical.

Mechanism for γ-radiation initiated graft copolymerization differs from the reactions carried-out in air and under vacuum, in the initiation step and can be presented as:

Initiation

$$nM \xrightarrow{\gamma-\text{Radiations}} {^*}M_n \quad (15)$$

$$H_2O \xrightarrow{\gamma-\text{Radiations}} H^* + {^*}OH \quad (16)$$

$$Psy - OH \xrightarrow{\gamma-\text{Radiations}} Psy - O^* + H^* \quad (17)$$

$$Psy - OH + {^*}OH \longrightarrow Psy - O^* + H_2O \quad (18)$$

$$M + {^*}OH \longrightarrow {^*}M - OH \quad (19)$$

$$Psy - OH + {^*}M - OH \longrightarrow Psy - O - M^* + H_2O \quad (20)$$
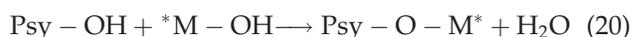
Propagation and termination follows the similar mechanism [eqs. (vii)–(xiv)].

A three dimensional network is formed as the multifunctional hexamethylene tetramine undergoes crosslinking with psyllium and monomer chains[32]:

Optimization of different reaction parameters

Effect of initiator concentration

Figure 2 depicts the effect of initiator concentration onto P_g. It has been observed that P_g increases with increase in initiator concentration but after reaching optimum level, it decreases. Optimum initiator
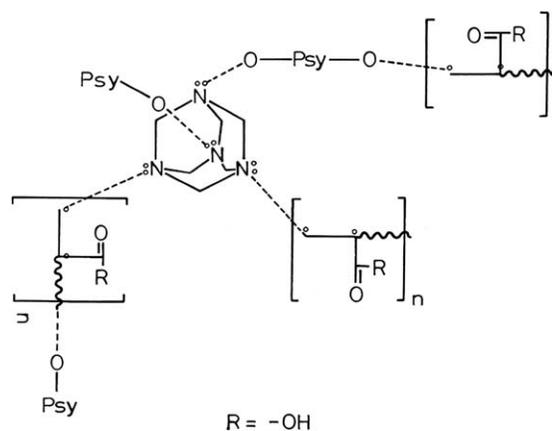
Figure 1 Crosslinked network of Psy-cl-poly(M).

Figure 3 Effect of amount of solvent on percentage grafting.

concentrations for getting maximum P_g in case of reactions conducted in air and under vacuum have been found to be 1.849×10^{-2} mol L^{-1} and 2.774×10^{-2} mol L^{-1}, respectively. It can be explained on the basis of the fact that with the increase in initiator concentration the concentration of free radicals on the activated chains increases which enhances the chance of collision between two radical species leading to termination.

Effect of solvent amount

It has been observed that initially P_g increases with increase in solvent amount (Fig. 3), but after reaching the maximum P_g, further increase in solvent resulted in decreased P_g. This can be explained on the basis that further increase in solvent amount results in decrease in concentration of OH* which ultimately decreased the free radical-sites on the back-bone and hence decreased P_g. Optimum solvent amount for the reactions carried-out in-air, in-

vacuum, and under γ-radiations was found to be 25 mL, 20 mL, and 20 mL, respectively.

Effect of reaction time

As is evident from Figure 4 that P_g increases with increase in reaction time and after reaching maximum, further increase in reaction time results in decreased graft-yield. This can be explained on the basis that after optimum reaction time homopolymerization predominates graft copolymerization. Optimum reaction time for getting maximum graft yield for the reactions carried-out in air (125%), in vacuum (138%) and under the influence of γ-radiations (124%) have been found to be 120, 240, and 600 min, respectively.

Figure 2 Effect of initiator concentration on percentage grafting.
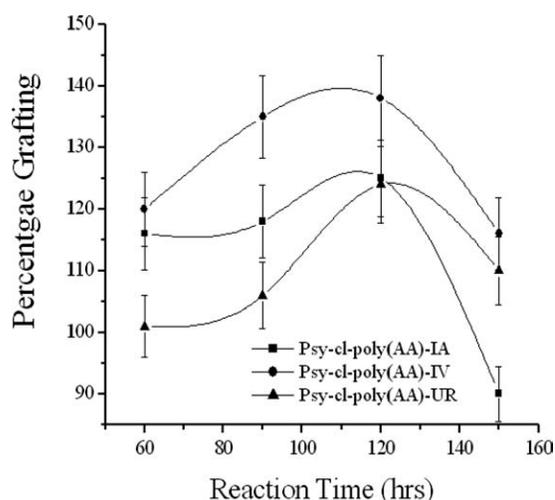
Figure 4 Effect of reaction time on percentage grafting.
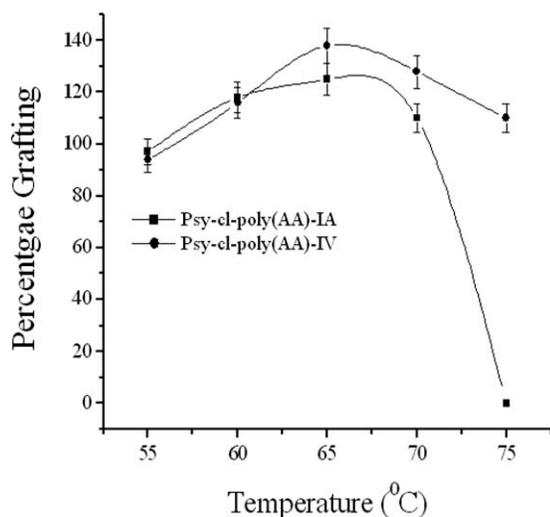
Figure 5 Effect of temperature on percentage grafting.

Effect of reaction temperature

It has been found that P_g increases with increase in reaction temperature both in case of reactions carried-out in air and in vacuum but after reaching the optimum temperature (65°C) further increase in temperature resulted in decreased graft yield (Fig. 5). It is due to the fact that kinetic energies of the free radicals increases with increase in temperature and beyond optimum temperature this increased kinetic energy resulted in increased collisions and termination reactions. Moreover, the hydrogen bonding weakens with increase in temperature resulting in shrinkage of hydrogels due to interpolymer chain association through the hydrophobic interactions.[33]

Effect of pH

It is evident from Figure 6 that maximum P_g in case of reactions carried-out in air, in vacuum and under
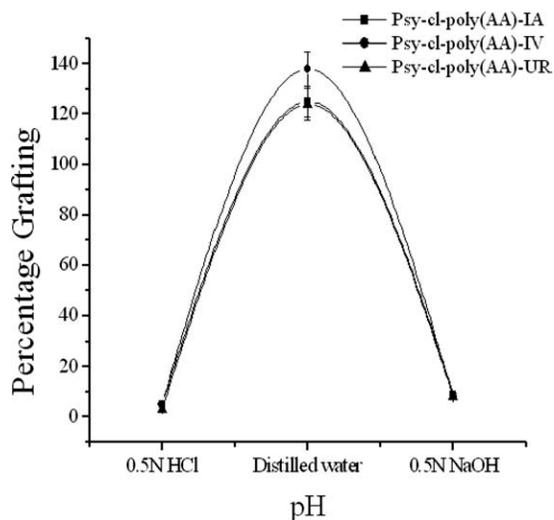
Figure 6 Effect of pH on percentage grafting.
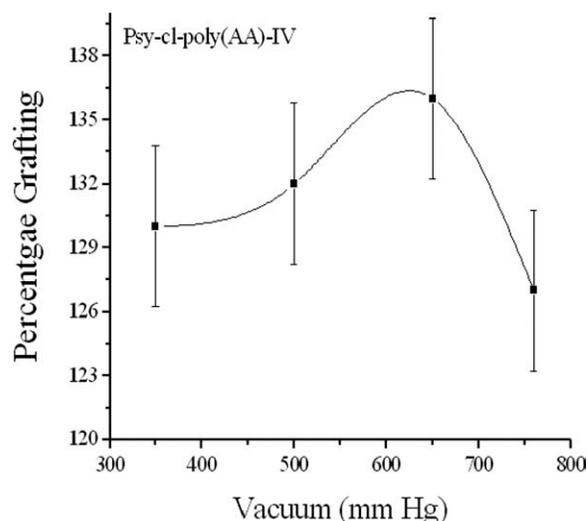
Figure 7 Effect of vacuum on percentage grafting.

the influence of γ-radiations has been found in neutral medium. However, in case of graft copolymerization carried-out in alkaline and acidic medium negligible graft yield was obtained. Moreover, it was observed that backbone polymer gets disintegrated under acidic and alkaline conditions. This could be the reason for minimum grafting under acidic and alkaline conditions.

Effect of vacuum and radiation dose

An increase in P_g with increase in vacuum up to 650 mmHg was observed (Fig. 7). However, further increase in vacuum resulted in decreased P_g. This could be due to frequent interactions between different chains free radicals resulting in the termination of the polymerization process [eqs. (xi) and (xii)]. In case of reaction carried-out in the presence of γ-radiations, P_g was found to increase with increase in radiation dose upto 25.92 kGy/h, and further increase in radiation dose resulted in decreased graft yield (Fig. 8). This is due to the fact that at higher radiation dose there is generation of more free radical sites on the backbone polymer and monomer moieties. Because of increased interactions between different free radical chain carriers, chain termination takes place and there is net decrease in graft yield.

Effect of monomer concentration

It is evident from Figure 9 that optimum concentration of acrylic acid for getting maximum P_s in case of reactions carried-out in air (3244), under vacuum (4325) and in the presence of γ-radiations (2175), has been found to be 5.8×10^{-1} mol L^{-1}, 3.625×10^{-1} mol L^{-1} and 7.25×10^{-1} mol L^{-1}, respectively. Further increase in monomer concentration resulted in
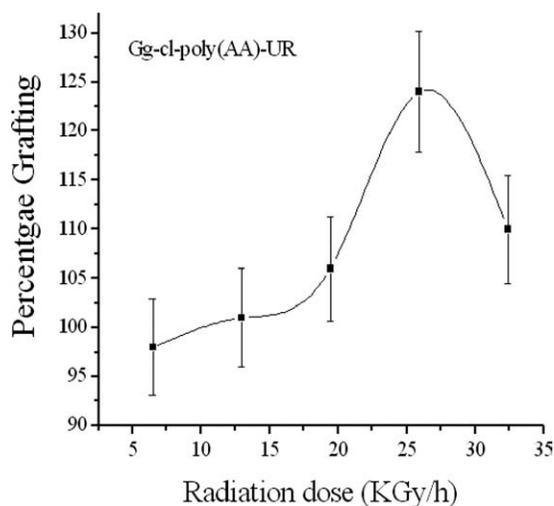
Figure 8 Effect of radiation dose on percentage grafting.

Figure 10 Effect of crosslinker concentration on percentage swelling.

decreased P_s which could be due to the reason that the viscosity of the medium increases with the increase in monomer concentration and it hinders the free movement of free radicals and monomer molecules.[34] Also the accessibility of more solvent into the polymeric matrices is prevented due to self-crosslinking reactions with increase in monomer concentration.

Effect of crosslinker concentration

It has been observed that P_s increases with increase in crosslinker concentration. However, after reaching the optimum level, further increase in crosslinker concentration resulted in decreased P_s (Fig. 10). This could be due to the reason that with increased crosslinker concentration, the crosslinking density increases resulting in decreased pore size, which leads to inaccessibility of the solvent molecules to

Figure 9 Effect of monomer concentration on percentage swelling.

enter the polymer matrix and hence decreased P_s. Optimum crosslinker concentrations for getting maximum P_s in case of reactions carried-out in air, in vacuum and under γ-radiations, were found to be 2.853×10^{-2} mol L^{-1} (3200), 1.783×10^{-2} mol L^{-1} (4380) and 7.133×10^{-2} mol L^{-1}, (10,578) respectively.

Comparative study of the Psy-cl-poly(AA) prepared in air, in vacuum and under the influence of γ-radiations

The graft copolymerization reactions were carried-out under three different conditions: in air, in vacuum and under the influence of γ-radiations. The optimized reaction parameters for getting maximum P_g or P_s, were found to be different for all the different reaction conditions. In-vacuum synthesis showed maximum P_g (138 ± 1.15) as compared with that of in-air (125 ± 1.00) and under the influence of γ-radiations (124 ± 1.15). The various optimized reaction parameters for the graft copolymerization and crosslinking carried-out under different reaction conditions are shown in Table II.

The minimum P_g observed in case of synthesis carried-out in air and under the influence of γ-radiations can be due to the action of oxygen as an inhibitor, decreasing the active free radical sites present on the backbone and acrylic acid and ultimately decreasing grafting.[35] The mechanism can be presented as:
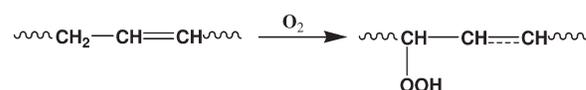
Hydroperoxide linkage decays with a following pathway:

Sample	[KPS] (mol/L)	Amount of solvent (mL)	Time (h)	Temp. (°C)	pH	[M] (mol/L)	[cl](mol/L)	Vacuum (mmHg)	Radiation Dose(kGy/h)
Psy-cl-poly(AA)- IA	0.01849	25.0	2.0	65	7.0	0.5800	0.02853	–	–
Psy-cl-poly(AA)-IV	0.02774	20.0	4.0	65	7.0	0.3625	0.01783	650	–
Psy-cl-poly(AA)-UR	–	20.0	10.0	–	7.0	0.725	0.07133	–	25.92

where, M, acrylic acid; cl, HMTA; KPS, Potassium persulphate; IA, in air; IV, in vacuum; UR, under radiations.
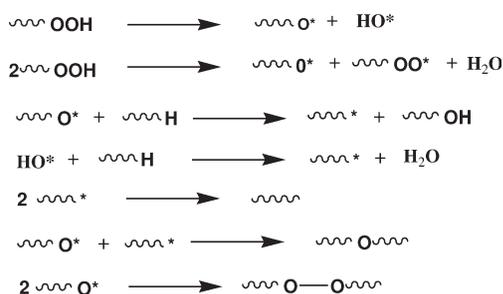
CHARACTERIZATION

FTIR spectroscopy

Psyllium

The IR spectrum of Psyllium showed broad peaks at 3780.9 cm^{-1} and 3427.6 cm^{-1} (O—H stretching bonded absorption of carbohydrates), 2925.8 cm^{-1}(CH$_2$ asymmetric stretching), 1378.8 cm^{-1}(CH, CH$_2$, and OH in-plane bending in carbohydrates), 1039.5 cm^{-1} (C—O stretching region as complex bands, resulting from C—O and C—O—C stretching vibrations), 897 cm^{-1} and 533 cm^{-1} (pyranose rings). Whereas, FT-IR spectrum of Psy-cl-poly(AA)-IA showed peaks at 2857.1 cm^{-1} (carboxylic acid O—H stretching), 1737.9 cm^{-1} (C=O stretching in carboxylic acid), 1636.4 cm^{-1} (strong C$^{......}$O asymmetric stretching) and 1400 cm^{-1} (coupled OH in-plane bending and C—O stretching) besides peaks obtained with that of Psyllium. IR spectrum of Psy-cl-poly(AA)-IV showed peaks at 2855.9 cm^{-1} (OH stretching of carboxylic acids), 2362.0 cm^{-1} (overtones and combinations of OH in-plane bending and C—O stretching vibration), 1744.1 cm^{-1} and 1659.6 cm^{-1} (C=O stretching in acids), 1440.6 cm^{-1}(coupled OH in-plane bending and C—O
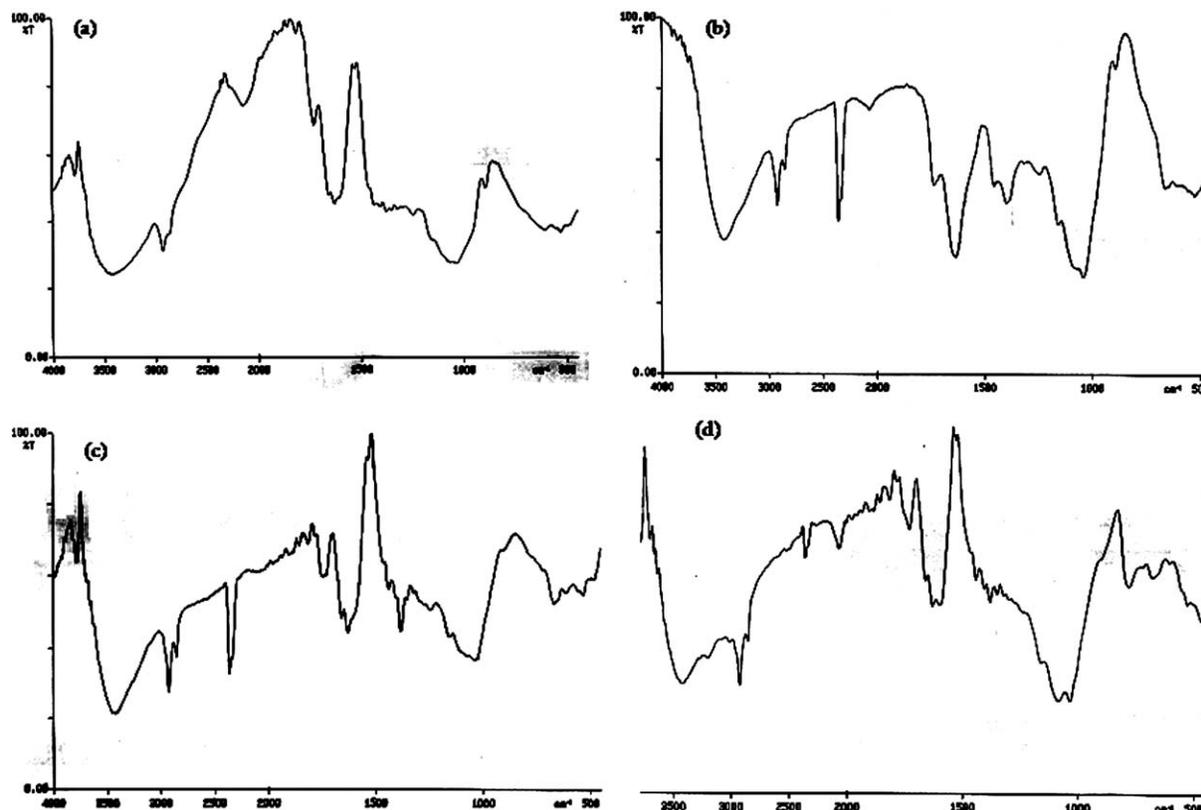
Figure 11 FT-IR of (a) Psyllium; (b) Psy-cl-poly(AA)-IA; (c) Psy-cl-poly(AA)-IV and (d) Psy-cl-poly(AA)-UR.
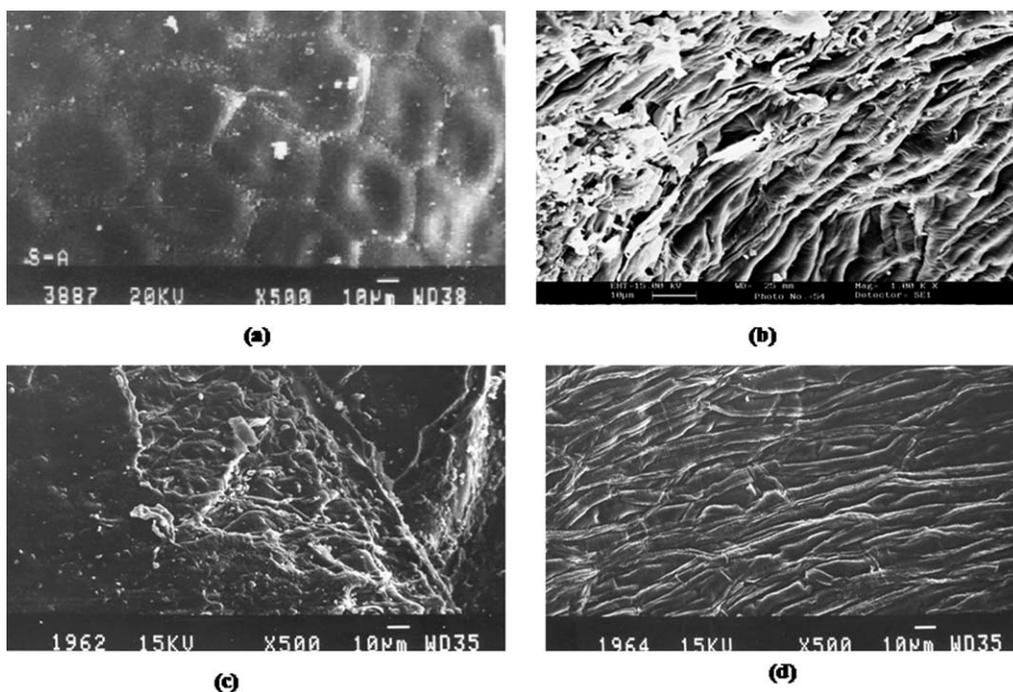
Figure 12 SEM of (a) Psyllium; (b) Psy-cl-poly(AA)-IA; (c) Psy-cl-poly(AA)-IV and (d) Psy-cl-poly(AA)-UR.
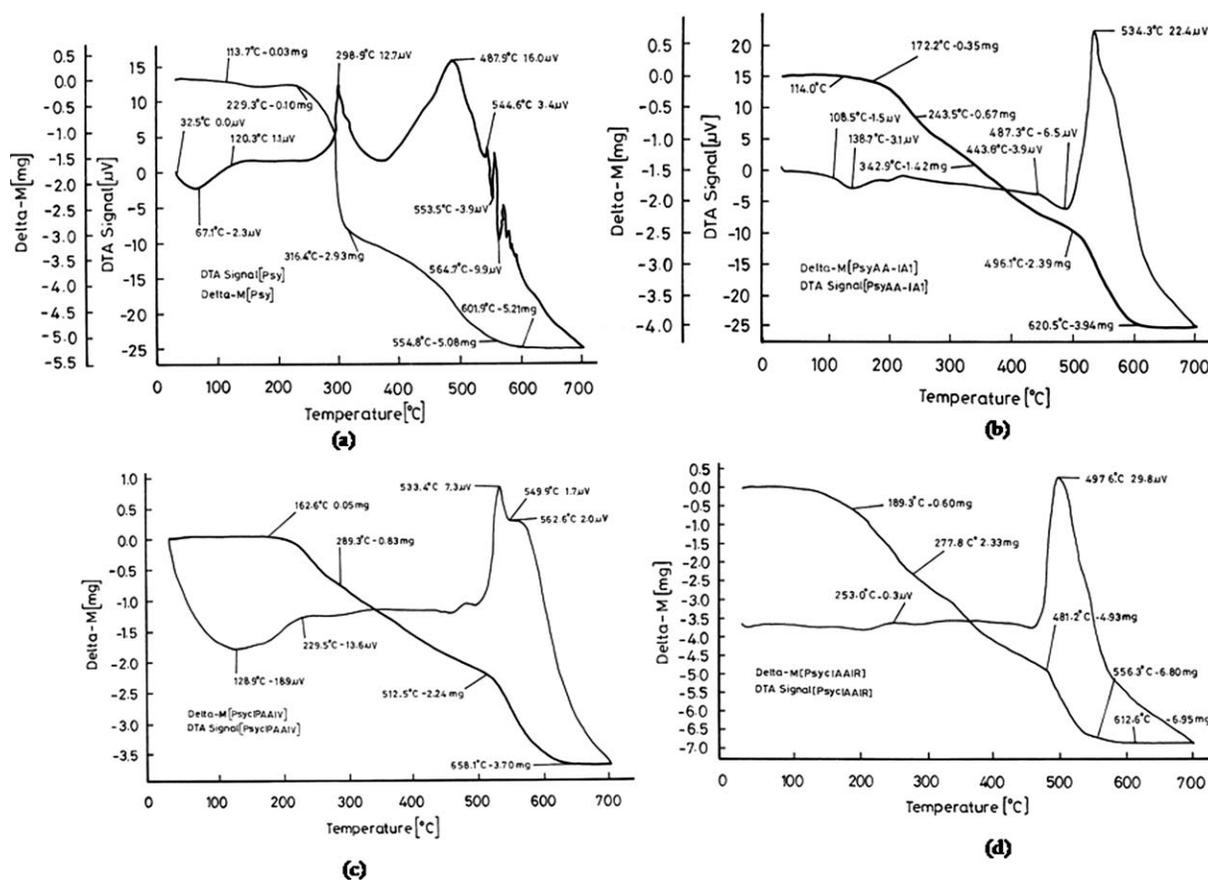
Figure 13 TGA/DTA of (a) Psyllium; (b) Psy-cl-poly(AA)-IA; (c) Psy-cl-poly(AA)-IV and (d) Psy-cl-poly(AA)-UR.

TABLE III
Percentage Crystallinity (%Cr) and Crystalline Index (C. I.) of Psyllium and Psy-cl-poly(AA) Prepared Under Different Reaction Conditions

Sample	P_g ± S. E.	At 2θ-scale		%Cr	C.I.
		$I_{21.297}$	$I_{34.744}$		
Psyllium	–	100	32	75.76	0.68
Psy-cl-poly(AA)-IA	125.0 ± 1.00	98	53	64.91	0.4592
Psy-cl-poly(AA)-IV	138.0 ± 1.15	88	33	72.73	0.6250
Psy-cl-poly(AA)-UR	124.0 ± 1.15	100	28	78.12	0.72

where, I, relative intensity; IA, in air; IV, in vacuum; UR, under radiations; P_g, percent grafting.

stretching) besides peaks obtained with that of Psyllium. IR spectrum of Psy-cl-poly(AA)-UR showed additional peaks at 2856.0 cm^{-1} (O—H stretching of carboxylic acid), 1731.3 cm^{-1} and 1631.8 cm^{-1} (C=O stretching in carboxylic acid) (Fig. 11).

Scanning electron microscopic studies

To have the conducting impact, the gels were gold plated and the scanning was synchronized with microscopic beam so as to maintain the small size over large distance relative to the specimen. The resulting images had a great depth of the field. A remarkable three dimensional appearance with high resolution was obtained in case of backbone and crosslinked samples. SEM results of Psyllium and crosslinked products of psyllium prepared under different reaction conditions clearly illustrate the niceties brought about by the graft copolymerization and crosslinking. The morphological changes in the features of Psyllium and functionalized Psyllium are quite evident (Fig. 12).

Thermogravimetric analysis and differential thermal analysis

Thermogravimetric analysis of Psyllium and Psy-cl-poly(M) in different conditions was carried-out as a function of percent weight loss versus temperature at a rate of 10°C/min in air. The analysis was performed to examine the changes in thermal properties
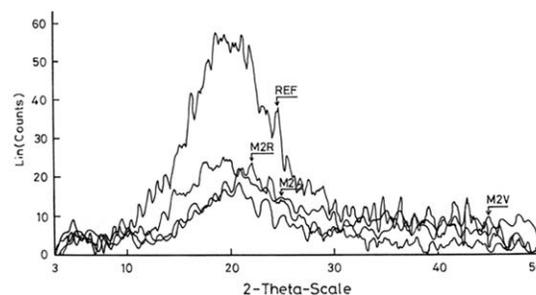
Figure 14 XRD of Psyllium and acrylic acid based hydrogels.

of the Psyllium brought about by graft copolymerization with acrylamide and acrylic acid in different reaction conditions.

Psyllium

It is quite evident from Figure 13(a) that Psyllium exhibited initial decomposition temperature (IDT) at 229.3°C and final decomposition temperature (FDT) at 601.9°C. Two stage decomposition has been found between 229.3°C to 316.4°C (wt. loss = 47.16%) and 316.4°C to 601.9°C (wt. loss = 38.0%). DTA curve of Psyllium indicated one endothermic peak at 67.1°C (−2.3 μV) and two exothermic peaks at 298.9°C (12.7 μV) and 487.9°C (6.0 μV).

Psy-cl-poly(AA)-IA

It has been found that in case of Psyllium, IDT (229.3°C) is higher as compared with that of Psy-cl-poly(AA)-IA (172.2°C). However, FDT of Psy-cl-poly(AA)-IA has been found to be higher (620.5°C) than that of Psyllium (601.9°C). Two-stage decomposition from 172.2°C to 496.1°C (wt. loss = 40.8%) and 496.1°C to 620.5°C (wt. loss = 31.0%) was observed [Fig. 13(b)]. DTA studies of this crosslinked sample showed one endothermic peak at 138.7°C (−3.1 μV) and one exothermic peak at 534.3°C (22.4 μV). It shows that exothermic combustion

TABLE IV
d-Spacings and Relative Intensities at Different 2θ-Values in Case of X-Ray Diffraction Studies of Psyllium and Psy-g-poly(AA) Prepared Under Different Reaction Conditions

Sample	P_g ± S.E	2θ-values									
		10.51		21.29		30.35		39.08		49.81	
		D	I	D	I	D	I	D	I	D	I
Psyllium	–	8.4128	20	4.1686	100	2.5799	22	2.3028	23	1.8291	04
Psy-g-poly(AA)-IA	125.0 ± 1.00	8.5438	37	4.2347	98	2.9903	62	2.3007	40	1.8417	03
Psy-g-poly(AA)-IV	138.0 ± 1.15	8.3403	17	4.3181	100	2.9673	57	2.2917	19	1.8345	06
Psy-g-poly(AA)-UR	124.0 ± 1.15	8.3813	39	4.0594	100	2.9581	38	2.2796	30	1.8324	00

where, D, d-spacings (°A); I, relative intensity; IA, in air; IV, in vacuum; UR, under radiations.

of Psy-cl-poly(AA)-IA persists at higher temperature as compared to that of Psyllium.[36]

Psy-cl-poly(AA)-IV

It is evident from Figure 13(c) that IDT and FDT of Psy-cl-poly(AA)-IV have been found to be 162.6°C and 658.1°C, respectively. In this case, two-stage decomposition from 162.6°C to 512.5°C (wt, loss = 45.8%) and 512.5°C to 658.1°C (wt. loss = 29.2%) has been observed. The results are further supported with DTA studies exhibiting exothermic peak at 533.4° (7.3 μV) and endothermic peak at 128.9° (−18.9 μV). It shows that exothermic combustion of Psy-cl-poly(AA)-IV persists at higher temperature as compared with that of Psyllium and accounts towards higher thermal stability.

Psy-cl-poly(AA)-UR

Psy-cl-poly(AA)-UR showed IDT and FDT at 189.3°C and 612.6°C, respectively. In this case, two-stage decomposition at 189.3°C to 481.2°C (wt. loss = 61.8%) and 481.2°C to 612.6°C (wt. loss = 28.8%) has been observed [Fig. 13(d)]. In DTA analysis, two exothermic peaks at 252.2°C (0.2 μV) and 499.8°C (29.9 μV) have been found. Thus, it is quite evident from the above results that the thermal stability of Psyllium could be increased through grafting and crosslinking.

X-ray diffraction

It has been observed that Psyllium exhibited 75.76% percentage crystallinity and crystalline index was found to be 0.6800. Whereas, Psy-cl-poly(AA)-IA, Psy-cl-poly(AA)-IV and Psy-cl-poly(AA)-UR exhibited 64.91%, 72.73%, and 78.12% percentage crystallinity, respectively. Crystalline indices of Psy-cl-poly(AA)-IA, Psy-cl-poly(AA)-IV, and Psy-cl-poly(AA)-UR have been found to be 0.4592, 0.6250, and 0.7200, respectively (Table III).

It is evident from Figure 14 that spectrum of Psyllium is more convex than that of all of the graft copolymers prepared under different reaction conditions. The incorporation of monomer moiety onto the Psyllium had impaired its crystallinity, thereby decreasing the %Cr.[30] However, Psy-cl-poly(AA)-UR showed exceptional behavior than that of others having more %Cr (78.12) than that of Psyllium. This exceptional behavior can be attributed to re-structuring of the crystal lattice during graft copolymerization under the influence of γ-radiations, leading to higher percentage crystallinity. The 2θ, I and d-values of graft copolymers have been found to be quite different than that of Psyllium (Table IV). In case of crosslinked moieties: Psy-cl-poly(AA)-IA, Psy-cl-poly(AA)-IV, and Psy-cl-poly(AA)-UR showed the relative intensities of 49 (d = 2.2175), 56 (d = 2.1085), and 30 (d = 2.2795), respectively, at 42.9° 2θ-scale. This behavior is due to the involvement of primary bonding like covalent bonding between Psyllium and acrylic acid during graft copolymerization.[26]

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