Gamma-Radiation Initiated Synthesis of *Psyllium* and Acrylic Acid-Based Polymeric Networks for Selective Absorption of Water from Different Oil–Water Emulsions

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ABSTRACT: Removal of water from the crude petroleum during its extraction and refining process is one of the major problems faced by petroleum industries, so in this study a superabsorbent has been synthesized from *Psyllium* and acrylic acid based polymers under the influence of gamma radiations using hexamine as a crosslinker. After optimizing various reaction parameters, the optimized superabsorbent has been tested for its selective water absorption capacity from different oil–water emulsions as a function of time, temperature, pH, and NaCl concentration. The synthesized superabsorbent has been found to be highly selective toward water absorption with maximum percent swelling of 8560% in petrol–water emulsion. © 2011 Wiley Periodicals, Inc. J Appl Polym Sci 124: 4969–4977, 2012

Key words: *Psyllium*; acrylic acid; oil–water emulsions; water absorption; gamma radiation

INTRODUCTION

Functionalized biopolymers have successfully taken over the era of synthetic polymers, for being cost-effective, biodegradable, environment friendly, and efficient. These biopolymers have been used in various applications such as waste-water treatment,[1] drug-delivery technology,[2,3] and membrane technology.[4] Various biopolymers have been previously modified and used efficiently as flocculants[5,6] and metal ion sorbents.[7,8] These modified biopolymers have also been used as adsorbents owing to their water absorbing capacity. Wang et al.[9] synthesized new hydrogels, loaded and unloaded with ammonium nitrate from acrylamide, acrylic acid, hydroxypropyl acrylate, and glycidyl methacrylate with ammonium persulfate as an initiator in water and ammonium nitrate solution. Nonloaded hydrogels showed greater swelling. In a study, crosslinked copolymers of acrylamide with calcium methacrylate were prepared using free radical copolymerization reaction in presence of N,N′-methylene-bis-acrylamide, 1,2-ethylene glycol dimethacrylate or diallyl phthalate crosslinkers, and ammonium persulfate-*N,N,N′,N′* tetramethylenediamine as a redox initiator. The product has further been investigated for its swelling and thermal characteristics.[10]

Keshava Murthy et al.[11] studied the preparation, swelling, and diffusion characteristics of starch and poly(acrylamide-*co*-sodium methacrylate) semi-interpenetrating networks. In another study, kinetics of swelling and dehydration of poly(vinyl alcohol)-poly(sodium acrylate) composite hydrogels has been investigated.[12] Orlov et al.[13] synthesized a series of polyelectrolytic hydrogels of N-isopropyl acrylamide with ionic monomer sodium methacrylate and studied its swelling behavior and effect of electric charge. Zhang et al.[14] prepared a starch phosphate-*graft*-acrylamide/attapulgite superabsorbent composite by graft copolymerization of starch phosphate, acrylamide, and attapulgite in aqueous solution and investigated the factors influencing water absorbency of the superabsorbent composite.

Caykara et al.[15] synthesized ionic hydrogels based on N,N-dimethylacrylamide, acrylamide, and itaconic acid by free radical crosslinking copolymerization in aqueous medium using ammonium persulfate-*N,N*-methylene-bis-acrylamide as an initiator-crosslinker system and analyzed the swelling behavior of these hydrogels at varied pH. Rodriguez et al.[16] investigated the swelling behavior of semi-interpenetrating polymer networks composed of poly(acrylamide) and poly(γ-glutamic acid) in water. Another study revealed the swelling behavior of N-isopropyl acrylamide hydrogels in aqueous solution of either

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TABLE I
Optimum Percent Grafting and Percent Swelling During Synthesis of Psy-cl-poly(AA)-UR

	Sample →	Psy-cl-poly(AA)-UR
P_g	M	124.0
	SE	1.15
	SD	2.00
P_s	M	10578.0
	SE	19.55
	SD	33.86

Where, no. of samples used in each case = 3; M = mean; SE = Standard error of mean; SD = standard deviation.

sodium chloride or di-sodium hydrogen phosphate.[17] Karadag et al.[18] investigated the swelling behavior of crosslinked acrylamide/maleic acid hydrogels synthesized by γ-radiation crosslinking in aqueous urea solutions. Orlov et al.[19] reported the swelling of nonionic N-isopropyl acrylamide hydrogels in aqueous solution of acetic acid or pyridine. Abd El-Rehim[20] explored the swelling behavior of radiation crosslinked acrylamide and acrylamide-Na-acrylate microgels.

Removal of water from the crude petroleum during its extraction and refining process is one of the major problems faced by petroleum industries. As it is quite evident from the literature survey that no work has been reported on the removal of water from crude petroleum–water emulsions through acrylic acid-*g*-*Psyllium* superabsorbents synthesized under the influence of γ-radiations. Therefore, in this research work, we have synthesized a superabsorbent from *Psyllium* and acrylic acid using radiation initiated graft copolymerization technique in presence of hexamine as a crosslinker and used it for the selective absorption of water from petrol–water, diesel–water, kerosene–water, and petroleum ether–water emulsions.

EXPERIMENTAL

Materials and method

Psyllium (Sidhpur Sat-Isabgol Factory, North Gujrat, India), acrylic acid (Merck-Schuchardt, Hohenbrunn, Germany), and hexamine (LOBA Chemie, Colaba, Mumbai, India) were used as received.

FTIR spectra of the samples were recorded on Perkin Elmer spectrophotometer using KBr pallets, LIBROR AEG-220 Shimadzu electronic balance was used for weighing purpose, Jeol Steroscan 150 Microscope was used for taking scanning electron micrographs (SEM). The samples were gold plated and the scanning was synchronized with microscopic beam so as to maintain the small size over a 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 crosslinked graft copolymerized superabsorbent. Linseis thermal analyzer was

used in air at a heating rate of 10°C/min for thermogravimetric analysis (TGA)/differential thermal analysis (DTA) analysis. X-ray diffraction studies of the samples were done on X-ray diffractometer (BRUKER AXS D8 ADVANCE). X-ray diffractions were performed under ambient conditions on Bruker-D_8 advance model using Cu Kα (1.5418 Å) 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 anti-scattering slit.

Synthesis of Psy-cl-poly(AA)

Psyllium (1.0 g) was added to the 10 mL of distilled water taken in the reaction flask. To the reaction mixture 3.625×10^{-1} mol L^{-1} of monomer was added and this was followed by the addition of crosslinker (7.133×10^{-2} mol L^{-1}) dissolved previously in minimum amount of the solvent. Mixture was made uniform by thorough stirring. The reaction was carried-out at room temperature (25°C) and under the influence of γ-radiations using Co-60 as the source of radiation. Various reaction parameters like radiation dose, amount of solvent, monomer concentration, and crosslinker concentration were optimized systematically. After completion of

TABLE II
Optimum Percent Swelling of Psy-cl-poly(AA)-UR During Swelling Studies in Different Petroleum Fraction–Water Emulsions

	Sample →	Psy-cl-poly(AA)-UR
Optimum P_s (Petrol–water)	M	8560.0
	SE	20.81
	SD	36.05
Optimum P_s (Diesel–water)	M	8230.0
	SE	15.27
	SD	26.45
Optimum P_s (Kerosene–water)	M	8140.0
	SE	25.16
	SD	43.58
Optimum P_s (Petroleum ether–water)	M	8200.0
	SE	20.81
	SD	36.05
Optimum P_s in brine solution (Petrol–water)	M	7320.0
	SE	15.27
	SD	26.45
Optimum P_s in brine solution (Diesel–water)	M	7110.0
	SE	20.00
	SD	34.64
Optimum P_s in brine solution (Kerosene–water)	M	6990.0
	SE	15.27
	SD	26.45
Optimum P_s in brine solution (Petroleum ether–water)	M	6970.0
	SE	20.81
	SD	36.05

Where, no. of samples used in each case = 3; M = mean; SE = standard error of mean; SD = standard deviation.

reaction, the homopolymer was removed by washings with water. The synthesized polymers were dried to constant weight in hot air oven at 50°C. Optimization of various reaction was carried-out as a function of percent grafting (P_g) and percent swelling (P_s) which were calculated as per the following method [eqs. (1) and (2)]:[21,22]

$$P_g = \frac{W_f - W_b}{W_b} \times 100 \qquad (1)$$

where W_f = weight of functionalized polymer, W_b = weight of backbone polymer.

$$P_s = \frac{W_s - W_d}{W_d} \times 100 \qquad (2)$$

where W_s and W_d are the weights of swollen polymer and dry polymer, respectively.

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.

Absorption of water from different oil–water emulsions

Different emulsions were prepared by mixing different petroleum fractions (petrol, diesel, kerosene, and petroleum ether) and water in 1 : 1 ratio (v/v). For the preparation of stable emulsion, tween-20 (10% of the total solution) was added to each solution as an emulsifier. Water absorption studies were carried-out by immersing 100 mg of hydrogel in each of petroleum fraction–water emulsion as a function of different time intervals (04, 08, 12, 16, and 24 h) and temperature (25, 30, 35, 40, 45, and 50°C), so as to get optimum time and temperature for maximum P_s. Weight of each sample was taken after a definite interval of time. Percent swelling (P_s) was calculated using eq. (2).

Moreover, water absorption studies from different petroleum fraction–water emulsions were also carried-out at varied pH (acidic, neutral, and alkaline) as well as at different concentrations of NaCl (1, 5, 10, and 15%), so as to find-out pH sensitive and salt resistant swelling of the hydrogel, at pre-optimized temperature and time conditions.

Statistical results of optimum percent swelling in different petroleum fraction–water and petroleum fraction–brine emulsions were calculated using SPSS version 10 (Table II).

RESULTS AND DISCUSSION

Psyllium consists of arabinoxylan which in turn is composed of straight polyxylopyranose chain with arabinofuranose branches at two or three positions.

—OH groups of arabinoxylan acts as active sites for the graft copolymerization reactions. The mechanism for the graft copolymerization of acrylic acid onto *Psyllium* is given in Scheme 1. Because of multi-functionality of hexamine, it undergoes crosslinking with *Psyllium* and monomer chains, thereby giving rise to a three dimensional network.[23]

Optimization of reaction parameters

Effect of radiation dose

Gamma radiations have been found to have a profound impact on the graft copolymerization of acrylic acid onto *Psyllium* backbone. Gamma radiation dose was varied from 6.48 to 32.4 KGy/H [Fig. 1(a)]. It was observed that percent grafting increases with increase in radiation dose up to 25.92 KGy/h and then decreases. Increase in radiation dose leads to increase in number of active sites and resulted in increased grafting. However, further increase in radiation dose after optimum is reached, resulted in decreased percentage grafting which could be due to the emergence of termination reactions. The live propagating chains on coming in contact resulting in the formation of dead polymeric chains and hence decreased grafting.[24,25]

Effect of amount of solvent

Figure 1(b) shows the effect of increase in amount of solvent onto percent grafting. As the amount of solvent increases, the P_g first increases and then decreases. This can be explained on the basis that with increase in amount of solvent, the concentration of *OH increases and are used for propagation of copolymerization reaction resulting in initial increase in P_g, however, further increase in amount of solvent results in increasing concentration of *OH which ultimately leads to termination (Eq. 12).[26]

Effect of monomer concentration

Monomer concentration was varied from 3.625×10^{-1} mol L^{-1} to 18.127×10^{-1} mol L^{-1}. It was found that the percent swelling first showed an initial increase up to 7.25×10^{-1} mol L^{-1} and then a decrease was observed. This is due to the fact that with increase in monomer concentration homopolymerization exceeds copolymerization [Fig. 1(c)]. Moreover, the viscosity of the reaction medium increases with increase in monomer concentration, thereby, hindering the free movement of free radicals and monomer molecules.[27]

Effect of crosslinker concentration

Figure 1(d) depicts the effect of crosslinker concentration onto percent swelling. It was observed that
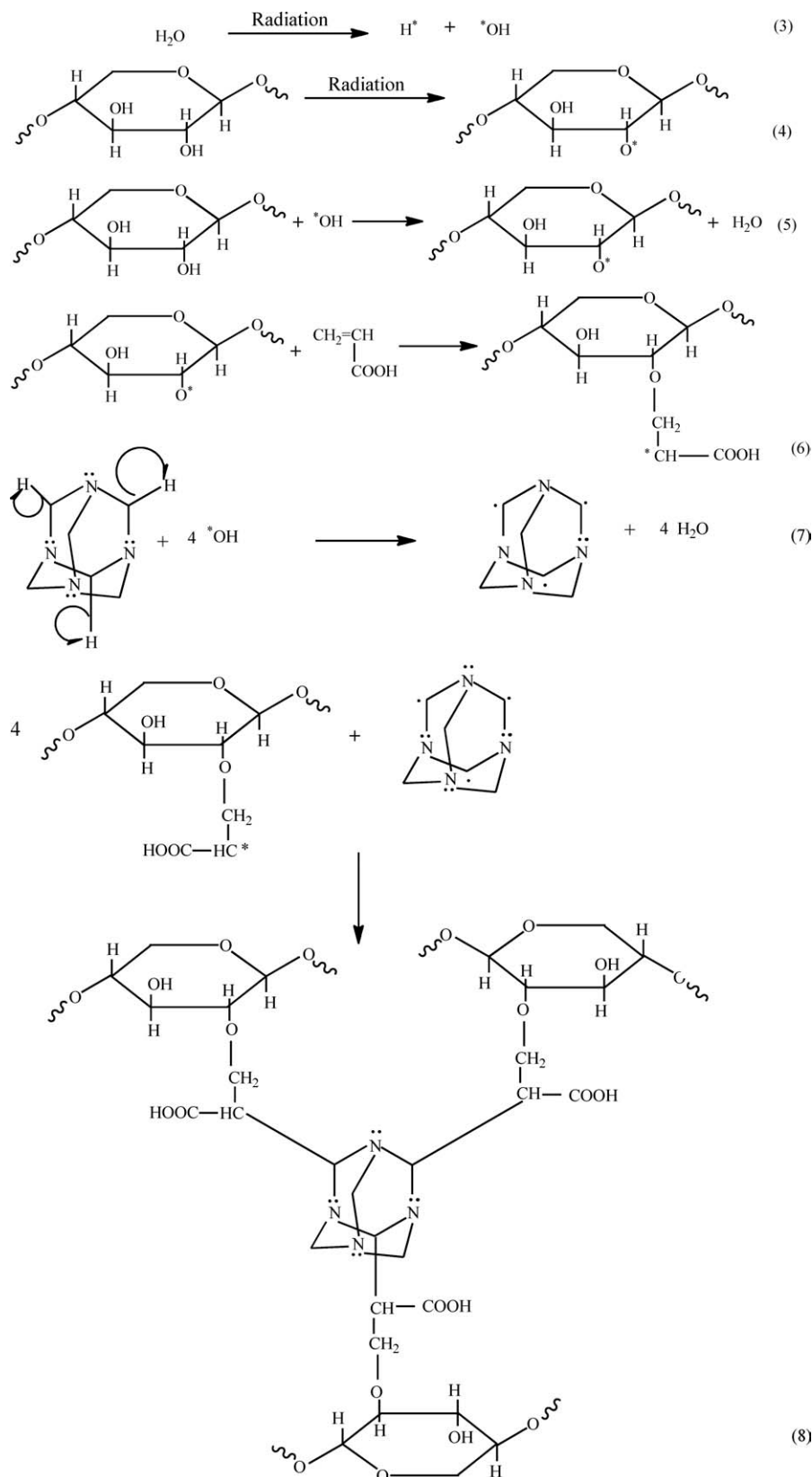
Scheme 1 Mechanism of graft copolymerization of *Psyllium* onto acrylic acid.

P_s increases with increase in crosslinker concentration but after reaching maximum at 7.133×10^{-2} mol L^{-1}, a decrease was noticed. It is due to the fact that at increased crosslinker concentration crosslinking density is more which leads to lesser approachability of solvent to the polymer matrix.[28]
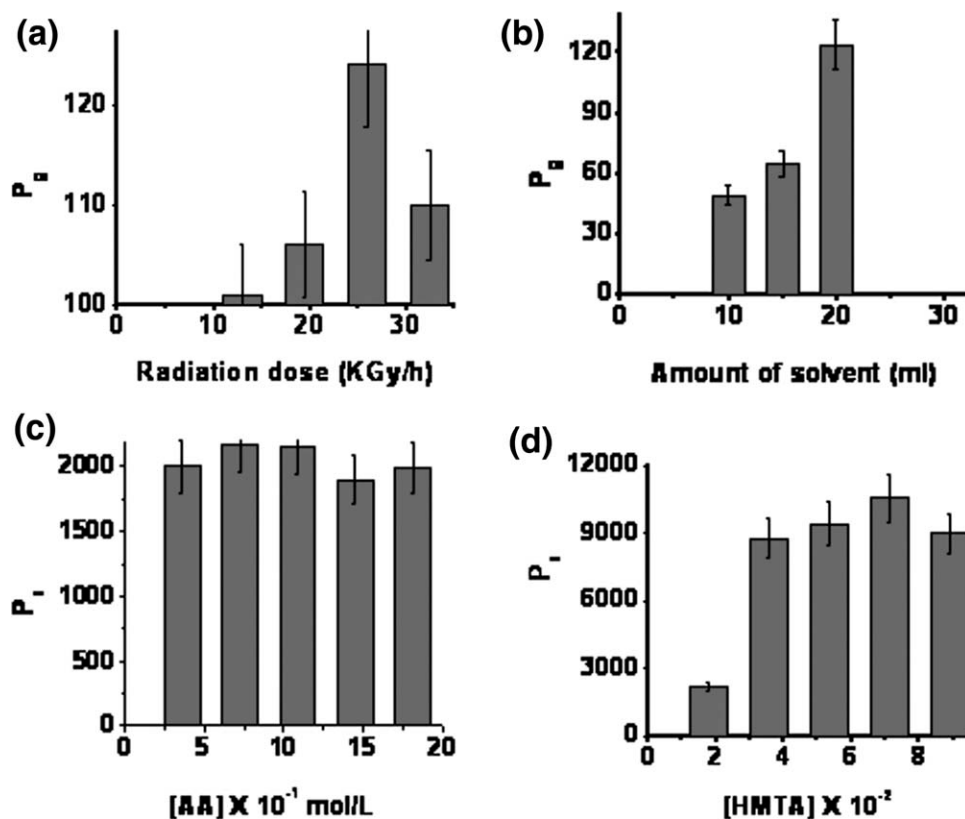
Figure 1 (a) Effect of reaction dose onto percent grafting. ([AA] = 0.725 mol/L, reaction time = 10 h-[UR]). (b) Effect of amount of solvent onto percent grafting. ([AA] = 0.725 mol/L, *Psyllium* = 1 g, reaction time = 10 h-[UR]). (c) Effect of AA concentration onto percent swelling. ([HMTA] = 0.01783 mol/L, reaction time = 10 h-[UR]). (d) Effect of crosslinker concentration onto percent swelling. ([AA] = 0.725 mol/L, reaction time = 10 h-[UR]).
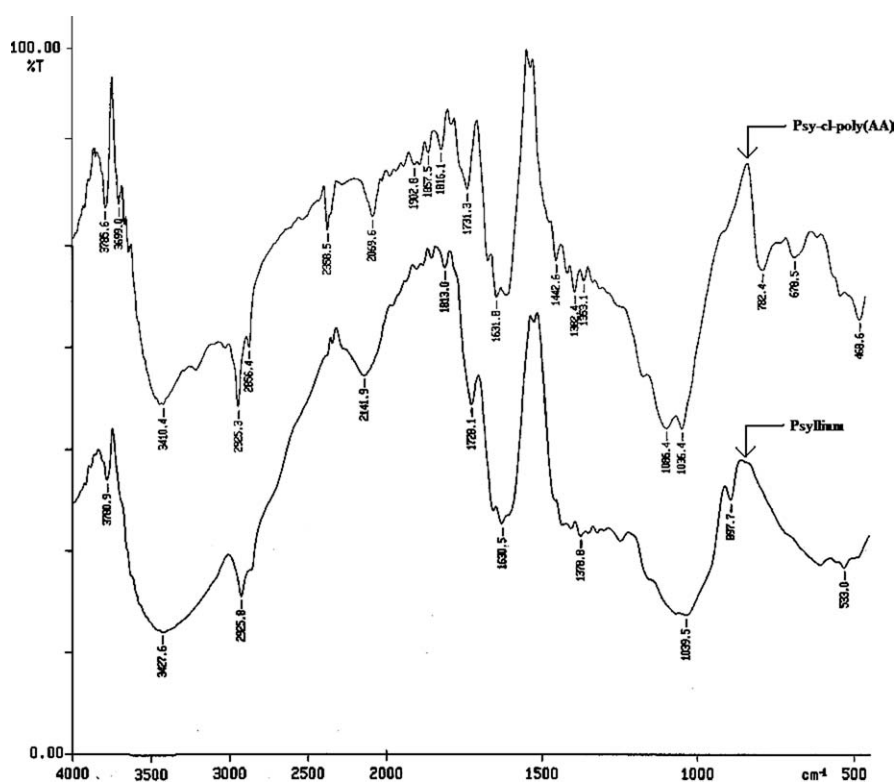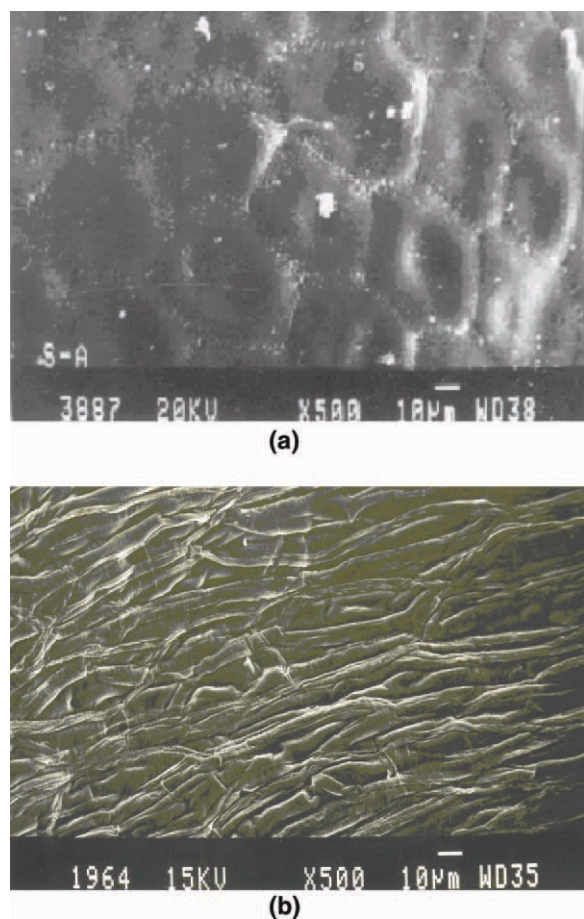

Figure 2 FT-IRs of *Psyllium* and Psy-cl-poly(AA).

Figure 3 (a) SEM of *Psyllium*. (b) SEM of Psy-cl-poly(AA). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Characterization

FTIR spectroscopy

IR spectrum of *Psyllium* showed 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) [Fig. 2(a)]. On the other hand, IR spectrum of Psy-cl-poly(AA) showed peaks at 2856.0 cm^{-1} (O—H stretching of carboxylic acid), 1731.3 cm^{-1} (C=O stretching in carboxylic acid) and 1631.8 cm^{-1} due to C=C stretching [Fig. 2(b)].

Scanning electron microscopy

Figures 3(a,b) exhibit the SEMs of *Psyllium* and Psy-cl-poly(AA), respectively. The morphological differences brought about by graft copolymerization

onto *Psyllium* can be clearly observed as the *Psyllium* showed homogeneous structure and Psy-cl-poly(AA) showed heterogeneous network structure.

TGA/DTA

TGA/DTA studies were performed as a function of percent weight loss versus temperature [Fig. 4(a,b)]. *Psyllium* shows initial decomposition temperature at 229.3°C and final decomposition temperature at 601.9°C while Psy-cl-poly(AA) synthesized under the influence of gamma radiations showed initial decomposition temperature of 189.3°C and final decomposition temperature of 612.6°C. Two-stage decomposition in both the cases was observed. *Psyllium* showed 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 (16.0 μV). On the other hand, Psy-cl-poly(AA) showed two exothermic peaks at 253.0°C (0.3 μV) and 497.6°C (29.8 μV). It is therefore, apparent from FDTs of *Psyllium* and Psy-cl-poly(AA) that the thermal stability of the polymer can be increased through grafting and crosslinking reactions.
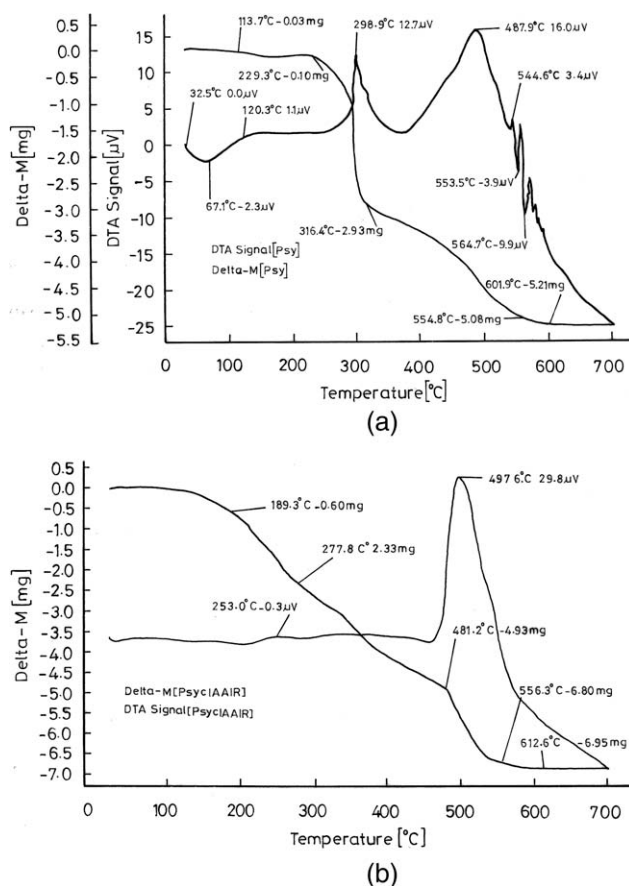

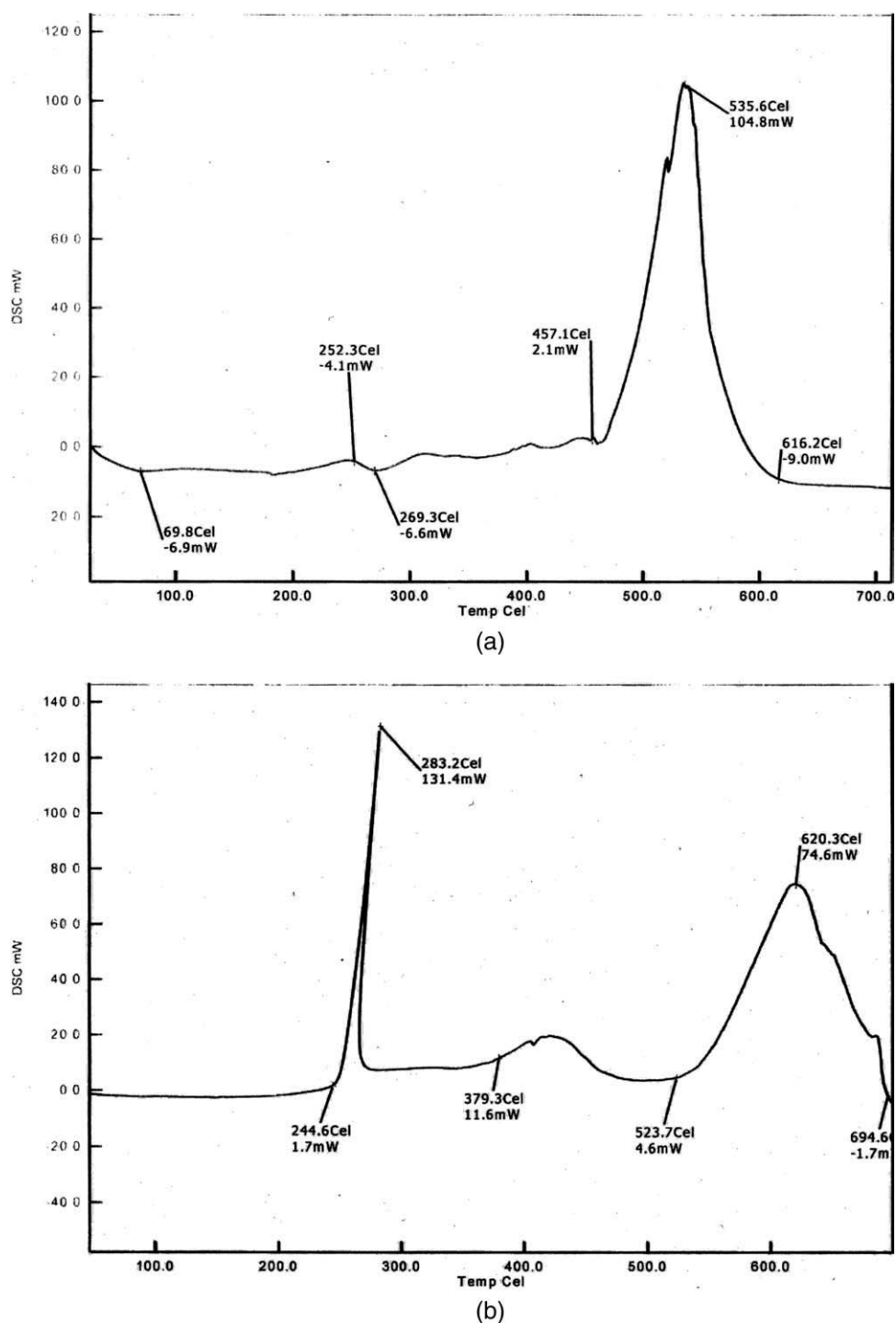**Figure 4** (a) TGA/DTA of *Psyllium*. (b) TGA/DTA of Psy-cl-poly(AA).

Figure 5 (a) DSC of *Psyllium.* (b) DSC of Psy-cl-poly(AA).

Differential scanning calorimetry

It is evident from the DSC studies that Psy-cl-poly (AA) is thermally more stable than the backbone [Fig. 5(a,b)]. *Psyllium* and Psy-cl-poly(AA) exhibited 457.1°C and 523.7°C as glass transition temperatures. Further, in case of *Psyllium*, exothermic peak was obtained at 535.6°C (104.8 mW), whereas Psy-cl-poly(AAm) showed exothermic peak at 620.3°C

(74.6 mW). Thus, DSC studies showed that the natural polysaccharide became thermally more stable after grafting and crosslinking.

X-ray diffraction studies

Coherence length (*L*) of the *Psyllium* and its graft copolymer was calculated using Scherrer equation:[29,30]

$$L = 0.9\lambda/\beta_{\frac{1}{2}}^{1} \times \cos\theta$$

where λ = wavelength, θ = diffraction angle, L = coherence length, and $\beta_{\frac{1}{2}}^{1}$ = full width half maximum.

It has been found that graft copolymerization of acrylic acid onto *Psyllium* resulted in increased coherence length with increase in graft copolymerization. Hence, there was net increase in anisotropy of the system with increase in graft yield (Table III).[30]

Water absorption studies from different oil–water emulsion studies

Effect of time onto percent swelling

Figure 6(a) depicts the effect of time onto P_s in different petroleum fraction–water emulsions at ambient temperature. The P_s increases with time and reaches a constant value after 24 h. At this temperature and time interval, the water absorption was found to be 8560, 8230, 8140, and 8200% in petrol–water, diesel–water, kerosene–water, and petroleum ether–water emulsions, respectively. This is due to the fact that after 24 h, the porous network of the absorbent got saturated with solvent molecules and is incapable of accommodating more solvent molecules.[26]

Effect of temperature onto percent swelling

As is evident from Figure 6(b), maximum P_s has been found at 25°C (8560, 8230, 8140, and 8200 in petrol–water, diesel–water, kerosene–water, and petroleum ether–water emulsions, respectively) and further increase in temperature resulted in decreased P_s. This can be explained on the basis that with increase in temperature the polymer got compacted resulting in decrease in pore size of the modified polymer, thereby leading to desorption.[31]

Effect of pH onto percent swelling

Maximum P_s has been observed in neutral medium, however, it was found that in alkaline and acidic media the polymer network got disintegrated which is due to the fact that the polymer matrix is not stable under such conditions.[26]
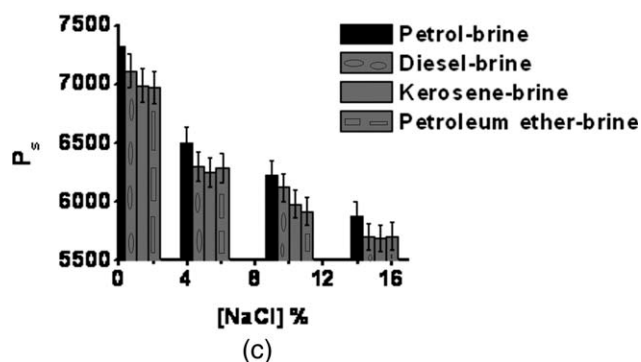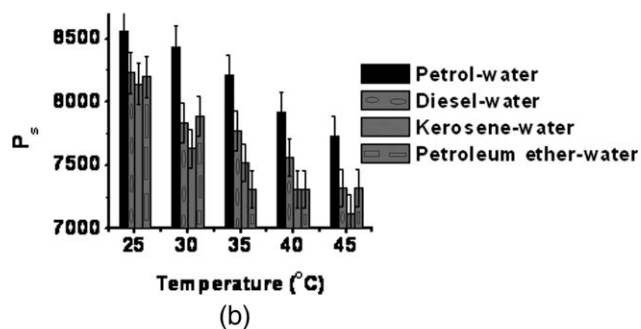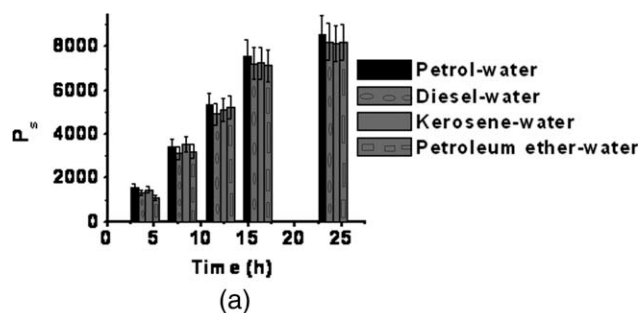

Figure 6 (a) Effect of time onto P_s of Psy-cl-poly(AA) in different petroleum fraction–water emulsions. (b) Effect of temperature onto P_s of Psy-cl-poly(AA) in different petroleum fraction–water emulsions. (c) Effect of NaCl concentration onto P_s of Psy-cl-poly(AA) in different petroleum fraction–brine emulsions.

Effect of NaCl concentration onto percent swelling

Figure 6(c) reveals that the candidate polymer exhibited maximum P_s in 1% NaCl concentration but with further increase in NaCl concentration there was decrease in P_s. Maximum water absorption of 7320, 7110, 6990, and 6970% was found in petrol–brine, diesel–brine, kerosene–brine, and petroleum ether–brine emulsions, respectively. It is due to the fact that at higher NaCl concentration desorption takes place due to reverse osmosis leading to lesser P_s.

CONCLUSION

The forgone study dealt with the synthesis of superabsorbent from *Psyllium* and acrylic acid based polymers under the influence of gamma radiations and

TABLE III
Effect of Concentration of Crosslinker on Coherence Length

Sample	Hexamine (mol L^{-1})	d-spacing	FWHM	Coherence length (nm)
Psyllium	–	4.1686	6.127	2.28
Psy-cl-poly(AA)	7.133×10^{-2}	4.3716	5.986	2.65

its application in selective absorption of water from different oil–water emulsions. It was found that the superabsorbent has tremendous water absorbing capacity and is sensitive toward pH as well as temperature. Since the superabsorbent was found to be selective toward water in all oil–water emulsions, and is therefore of great industrial importance.

References

1. Mishra, A.; Bajpai, M. J Hazard Mater 2005, 118, 213.
2. Sen, G.; Pal, S. Int J Biol Macromol 2009, 45, 48.
3. Rana, V.; Rai, P.; Tiwary, A. K.; Singh, R. S.; Kennedy, J. F.; Knill, C. J. Carbohydr Polym 2011, 83, 1031.
4. Huang, J.; Wang, X. I.; Yu, X. H. Desalination 2006, 192, 125.
5. Tripathy, J.; Mishra, D. K.; Yadav, M.; Behari, K. Carbohydr Polym 2010, 79, 40.
6. Ghosh, S.; Sen, G.; Jha, U.; Pal, S. Bioresource Technol 2010, 101, 9638.
7. Sand, A.; Yadav, M.; Behari, K. Carbohydr Polym 2010, 81, 626.
8. Sand, A.; Yadav, M.; Mishra, M. M.; Tripathi, J.; Behari, K. Carbohydr Polym 2011, 83, 14.
9. Wang, H.; Wang, Z.; Zhu, B. React Funct Polym 2007, 67, 225.
10. Murali Mohan, Y.; Keshava Murthy, P. S.; Sreedhar, B.; Mohana Raju, K. J Appl Polym Sci 2006, 102, 1.
11. Keshava Murthy, P. S.; Murali Mohan, Y.; Sreeramulu, J.; Mohana Raju, K. React Funct Polym 2006, 66, 1482.
12. Graiver, D.; Hyon, S-H.; Ikada, Y. J Appl Polym Sci 2003, 57, 1299.
13. Orlov, Y.; Xu, X.; Maurer, G. Fluid Phase Equilibr 2006, 249, 6.
14. Zhang, J.; Li, A.; Wang, A. Carbohydr Polym 2006, 65, 150.
15. Caykara, T.; Kiper, S.; Demirel, G. Eur Polym J 2006, 42, 348.
16. Rodriguez, D. E.; Romero-Garcia, J.; Ramirez-Vargas, E.; Ledezma-Perez, A. S.; Arias-Marin, E. Mater Lett 2006, 60, 1390.
17. Orlov, Y.; Xu, X.; Maurer, G. Fluid Phase Equilibr 2007, 254, 1.
18. Karadag, E.; Uzum, O. B.; Saraydin, D.; Guven, O. Mater Design 2006, 27, 576.
19. Orlov, Y.; Xu, X.; Maurer, G. Fluid Phase Equilibr 2005, 238, 87.
20. Abd El-Rehim, H. A. Radiat Phys Chem 2005, 74, 111.
21. Kaur, I.; Chauhan, G. S.; Misra, B. N.; Gupta, A. Desalination 1997, 110, 129.
22. Chauhan, G. S.; Guleria, L. K.; Mahajan, S. Desalination 2001, 141, 325.
23. de Bruyn, P. J.; Gable, R. W.; Potter, A. C.; Solomon, D. H. Acta Crystallogr C 1996, 52, 466.
24. Kaur, I.; Singh, B.; Gupta, N. Radiat Phys Chem 2005, 72, 489.
25. Singh, B.; Kumar, S. Nucl Instrum Meth B 2008, 266, 3430.
26. Kaith, B. S.; Kumar K. e-Polymers 2007, No.002.
27. Pourjavadi, A.; Mahdavinia, G. R. Turk J Chem 2006, 30, 595.
28. Xu, F-J.; Kang, E-T.; Neoh, K-G. Biomaterials 2006, 27, 2787.
29. Patteron, A. L. Phys Rev 1939, 56, 978.
30. Malik, H.; Gupta, N.; Sarkar, A. Mater Sci Eng C 2002, 20, 215.
31. Zhang, X. Z.; Yang, Y. Y.; Chung, T. S.; Ma, K. X. Langmuir 2001, 17, 6094.