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In Vacuum Preparation of Psy-cl-poly(AAm) Superabsorbent and its Applications in Oil - Industry

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Abstract: In the present study *Psyllium* was modified with acrylamide through chemically induced graft co-polymerization, under the influence of vacuum using potassium persulphate as an initiator. Graft copolymers were further crosslinked with hexamethylene tetramine for their application in removal of water from different water-oil emulsions. The hydrogel was found to be selective in its absorption and maximum absorption of water was found to be 3020%.

Keywords: Psyllium, acrylamide, water absorption, water-oil emulsions.

Introduction

Polymers obtained from natural sources have widened usability in diversified fields. They are not only efficient in different applications but cost-effective, environment friendly and bio-degradable as well. Many workers have successfully modified various natural polysaccharides such as chitosan [1], pectin [2], starch [3, 4], gelatin [5], cellulose [6] and psyllium [7] through grafting and crosslinking reactions for use in various industrially important fields.

Three-dimensional crosslinked polymeric networks also known as ‘hydrogels’ can absorb water many times their own weight and are known as ‘superabsorbent’. Due to their swelling properties and environment sensitivity these hydrogels are finding great use as sensors, separation membranes, adsorbents and in drug delivery systems. Water absorbancy can be a criterion for the characterization of swelling properties of superabsorbent polymers [8-16]. Psyllium is a natural polysaccharide which is obtained from natural plant species *plantago ovata*. Psyllium husk forms mucilage composed of arabinoxylan (arabinose 22.6%, xylose 74.6%) [17] and it is well known for its medicinal importance. It is being used against various diseases such as diabetes, constipation, diarrhea and high cholesterol level.

Keeping in view the mucilage property and water absorbancy characteristic of *Psyllium*, in the present investigation, a cross-linked three dimensional net-work of it with acrylamide has been synthesized using potassium persulphate-hexamethylene tetramine as an initiator-crosslinker system. The network polymers formed were further tested for their water removal capacity in different water-oil emulsions.

Results and Discussion

Hydroxyl groups present in the arabinoxylan (composed of xylose straight chain with arabinose branches at 2 or 3 positions), a mucilage forming fraction of

Psyllium, are the active sites for the graft co-polymerization of poly(AAm) onto it and can be presented through the following mechanism:

Initiation

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

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

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

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

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

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

Propagation

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

$$Psy-O-M^{*}+nM \rightarrow Psy-O-(M)_n-M^{*} \quad (8)$$

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

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

Termination

$$Psy-O-(M)_n-M^{*}+M^{*}-(M)_n-O-Psy \rightarrow Psy-O-(M)_n-M_2-(M)_n-O-Psy \quad (11)$$

Graft co-polymer

$$Psy-O-(M)_{n-1}-M^{*}+M^{*}-(M)_{n-1}-O-Psy \rightarrow Psy-O-(M)_{n-1}-M_2-(M)_{n-1}-O-Psy \quad (12)$$

Graft co-polymer

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

$$HO-(M)_n-M^{*}+{}^{*}M-(M)_n-OH \rightarrow HO-(M)_n-M_2-(M)_n-OH \quad (14)$$

Homopolymer

M^{*} = *Monomer free radical,* $Psy-O^{*}$ = *Backbone free radical*

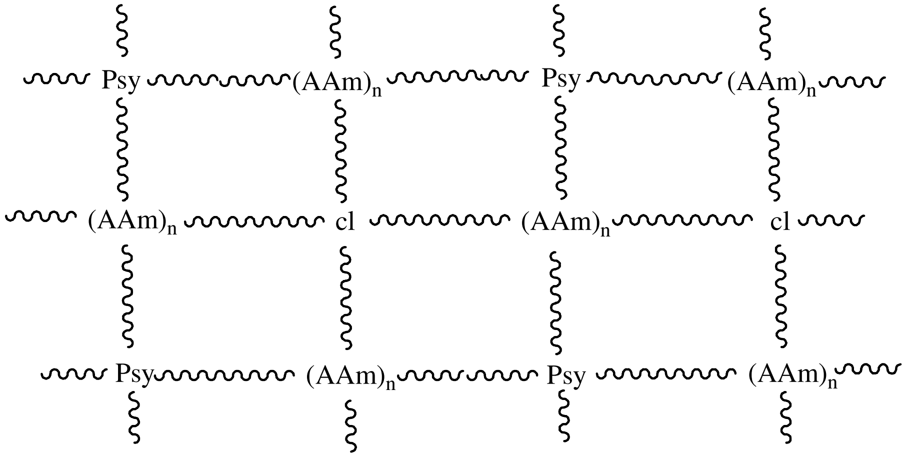
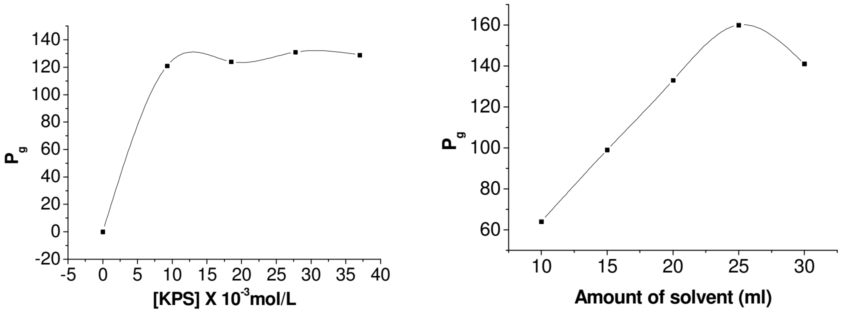


Fig. 1. Inter-Penetrating Network of Psy-cl-poly(AAm) where cl = cross-linker; $(AAm)_n$ = polyacrylamide chain; Psy = Psyllium.

Because of multi-functionality of Hexamethylene tetramine, it can form a networking with *Psyllium* and poly(AAm) chains, thereby giving rise to a three dimensional network as follows:

Optimization of different reaction parameters

As is evident from Fig 2a, P_g increases with increase in initiator concentration and the optimum concentration for maximum P_g (131%) was found to be 2.774 $\times 10^{-2}$ molL^{-1}. Beyond this concentration P_g decreases which is due to the predominance of homo-polymerization over graft co-polymerization [18].



(a) (b)

Fig. 2. (a) Effect of initiator concentration onto percent grafting. ([AAm]=0.703 mol/L, Psyllium=1g, reaction time=02h, reaction temperature= 65\+(o)C.) (b) Effect of amount of solvent on to percent grafting. ([AAm]=0.703 mol/L,[KPS]= 0.00924 mol/L, Psyllium=1g, reaction time=02h, reaction temperature= 65\+(o)C.)

Amount of solvent is found to play an important role in graft co-polymerization. Maximum P_g (160%) is found with 25 ml of the solvent and further increases in volume results in decreased P_g. This can be explained on the basis that there lies sufficient concentration of *OH for propagating the polymerization reaction and further increase in volume of the solvent results in termination of polymerization (Fig. 2b, equation 13).

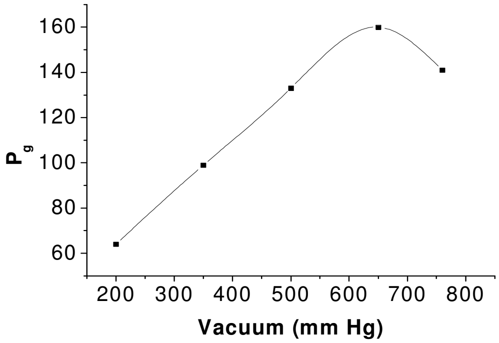
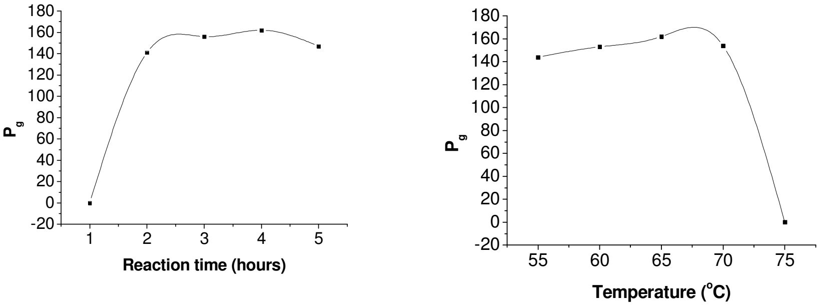


Fig. 3. Effect of vacuum on to percent grafting. ([AAm]=0.703 mol/L,[KPS]= 0.00924 mol/L, Psyllium=1 g, reaction time=02 h, reaction temperature= 65\+(o)C.)

Fig. 3 depicts the effect of increase in vacuum on P_g of the polymer obtained. It was observed that the P_g increases with increase in vacuum up to 650mmHg and decreases thereafter. This can be due to the fact that under high vacuum there are more chances of interaction between the free radical species thereby resulting in the formation of dead polymer (equations 11 & 12).

Figs. 4a and 4b exhibits that P_g increases with increase in reaction time and temperature. Optimum reaction time and temperature for maximum P_g (162%) have been found to be 240 minutes and 65℃ respectively. However, further increase in reaction time and temperature results in decreased P_g. This could be due to predominance of homo-polymerization over graft co-polymerization (equations 5 & 6) [18].



(a) (b)

Fig. 4. (a) Effect of reaction time on to percent grafting. ([AAm]=0.703 mol/L,[KPS]= 0.00924 mol/L, Psyllium=1g, reaction temperature= 65\+(o)C.) (b) Effect of temperature onto percent grafting. ([AAm]=0.703 mol/L,[KPS]= 0.00924 mol/L, Psyllium=1g, reaction time=02h.)

Fig. 5 shows that the co-polymerization reaction takes place only in neutral medium and not in alkaline and acidic media. In acidic medium it could be due to the neutralization of hydroxyl ions with H^+ ions, thereby resulting in decrease in production of free radical sites on back-bone. On the other hand, in case of alkaline medium excess of *OH groups results in early initiation of termination reactions (equation 13) [19].

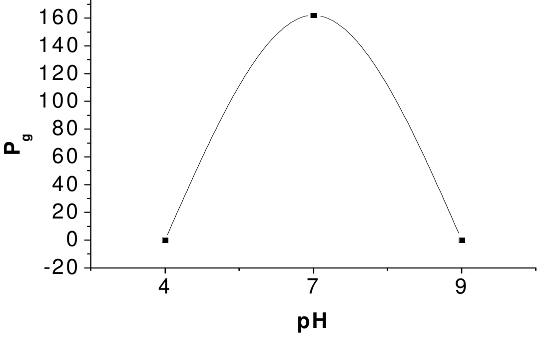
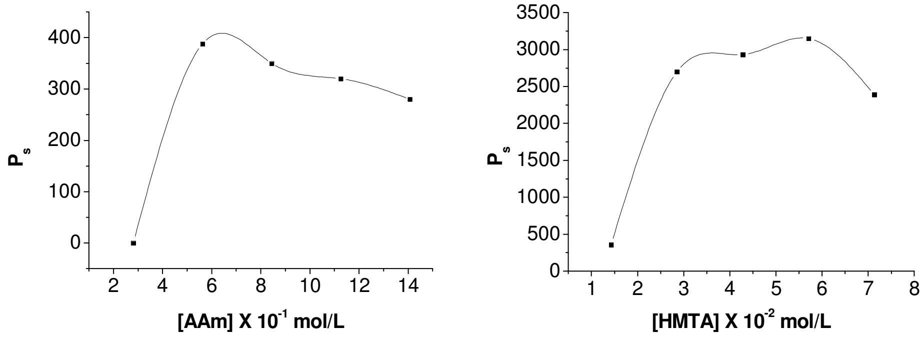


Fig. 5. Effect of pH onto percent grafting. ([AAm]=0.703 mol/L,[KPS]= 0.00924 mol/L, Psyllium=1g, reaction time=02h, reaction temperature= 65\+(o)C.)

It has been observed that maximum water uptake (388%) of the hydrogel formed is with 5.624 $\times 10^{-1}$ $molL^{-1}$ concentration of AAm, beyond which water absorption decreases. It can be due to the fact that further increase in monomer concentration results in more compact structure with less porosity, thereby resulting in less water absorption. (Fig. 6a).



(a) (b)

Fig. 6. (a) Effect of AAm concentration onto percent swelling. ([KPS]=0.00924 mol/L, [HMTA]=0.05706 mol/L, Psyllium=1 g, reaction time=02 h, reaction temperature= 65\+(o)C). (b) Effect of crosslinker concentration onto percent swelling. ([AAm]=0.5624 mol/L,[KPS]= 0.00924 mol/L, Psyllium=1 g, reaction time=02 h, reaction temperature= 65\+(o)C).

As is evident from Fig. 6b, with increase in crosslinker concentration, water absorption increases and maximum water absorption (3020%) is found at 5.706 $\times 10^{-2}$ $molL^{-1}$. Further increase in concentration results in decreased water absorption. It can be explained on the basis that more increase in crosslinker concentration results in more dense three dimensional structures with excess cross-linking thereby leaving little space for water absorption.

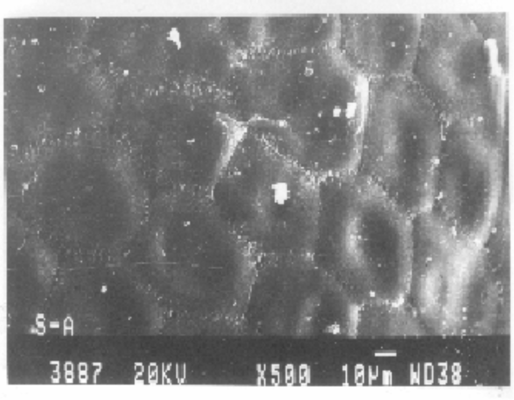
FTIR Spectroscopy

The IR spectrum of psyllium shows 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).

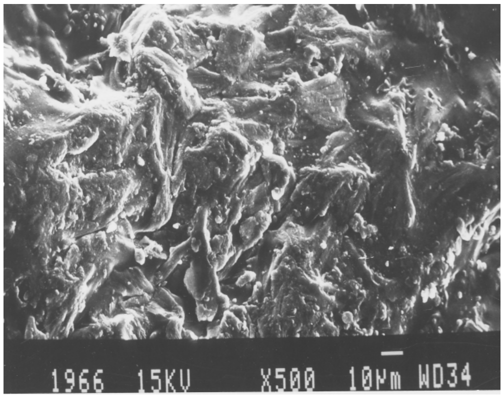
On the other hand, IR spectrum of Psy-cl-poly(AAm) showspeaks at 3888.7 cm^{-1}(polymeric hydroxyl compound), 3664.9 cm^{-1}(N-H stretching vibrations), 1668.0 cm^{-1}(C=O stretching of amide I band), 1433.8 cm^{-1} (N-H in-plane bending of Amide II band), 1246.4 cm^{-1}(C-N stretching vibrations of Amide III band) and 617.7 cm^{-1}(OCN deformations of amide IV band) besides, peaks of psyllium.

Scanning Electron Microscopic Studies of Gels

To have the conducting impact, the gels are gold plated. In order to maintain the small size over large distance relative to the specimen, the scanning is synchronized with microscopic beam. The resulting images have a great depth of the field. A remarkable three dimensional appearance with high resolution is obtained. SEM results of the psyllium and Psy-cl-poly(AAm) illustrate and magnify the intricacies brought about by the graft co-polymerization and crosslinking. It is quite evident from scans that morphological changes in features of the psyllium have taken place after grafting and networking (Figs. 7a-7b).



(a)



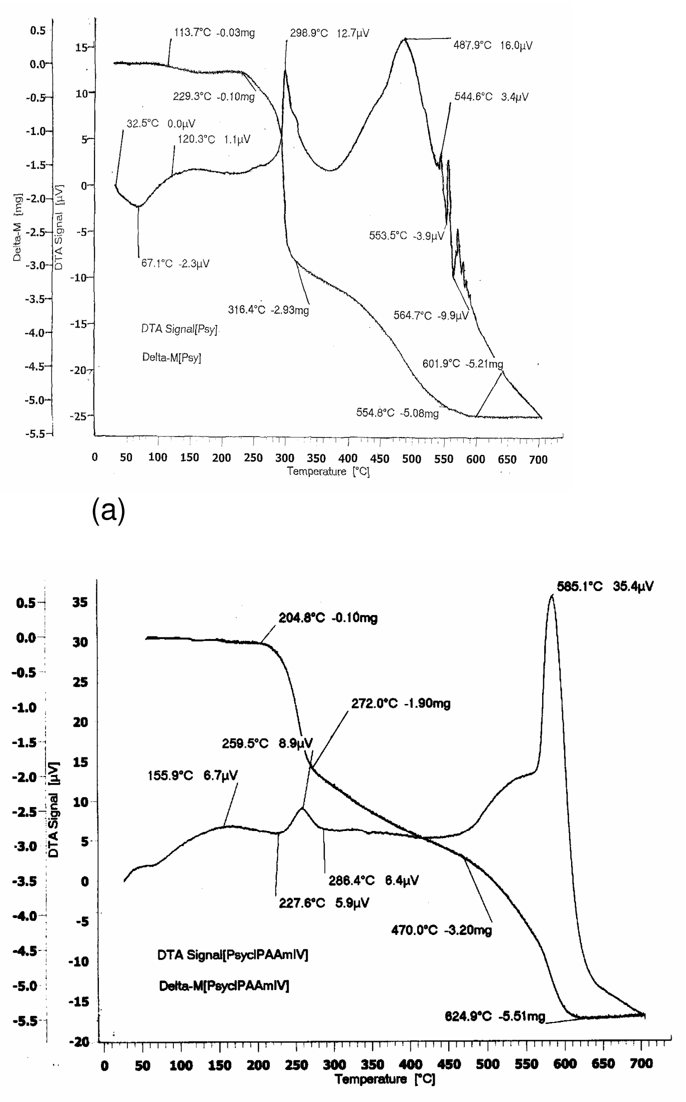
(b)

Fig. 7. (a) SEM of Psyllium (b) SEM of Psy-cl-poly(AAm).

Thermal Behavior of Gels

Thermo-gravimetric analysis of both psyllium and Psy-cl-poly(AA) is carried-out as a function of percent weight loss versus temperature. It has been found that in case of psyllium, initial decomposition temperature (229.3ºC) is higher as compared to that of Psy-cl-poly(AAm) (204.8ºC). This appears due to initial disturbance in the crystalline lattice of the backbone during graft co-polymerization. However, final decomposition temperature of Psy-cl-poly(AAm) has been found to be higher (624.9ºC) than that of psyllium (601.9ºC). This shows that on crosslinking of psyllium with AAm-HMTA, it becomes thermally more stable. In both the cases two-stage decomposition has been observed (Figs. 8a and 8b).

The results are further supported with DTA studies. In case of psyllium one endothermic peak at 67.1ºC (-2.3 µV) and two exothermic peaks at 298.9 ºC (12.7 µV) and 487.9ºC (16.0 µV) have been observed. Whereas in case of Psy-cl-poly(AAm), two exothermic peaks at 259.5ºC (8.9µV) and 585.1ºC (35.4µV) have been found. It shows that exothermic combustion of Psy-cl-poly(AAm) persists at higher temperature as compared to that of psyllium.



(a)

(b)

Fig. 8. (a) TGA of Psyllium (b) TGA of Psy-cl-poly(AAm).

Water absorption studies in oil-water emulsions

-Effect of time onto percent swelling

Water uptake studies are carried-out at different time intervals (04, 08, 12, 16 and 24 hs). P_s increases with increase in time but its rate start decreasing after 12 hours and attains a constant value after 24 hours (Fig. 9a). It can be due to the fact that active sites for absorption get fully saturated with the solvent thereby blocking any scope for further absorption. 100 mg of sample is found to remove 5.92, 6.10, 7.15

and 6.82% of water from 80 ml of each petrol-water, diesel-water, kerosene-water and petroleum ether-water emulsions, respectively (Table-1).

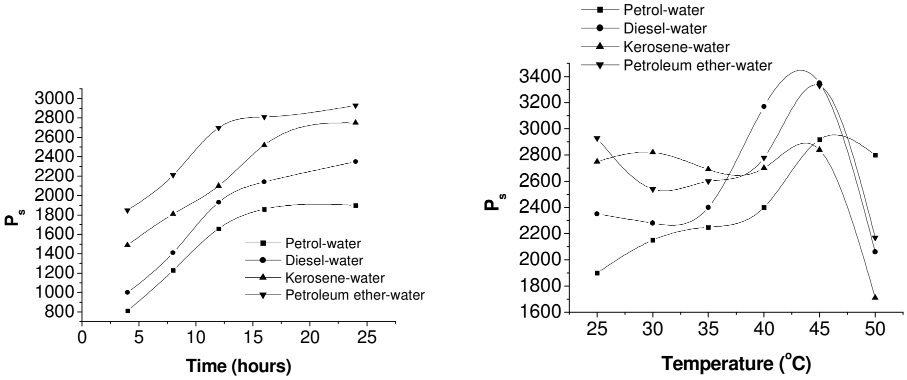


Fig. 9. (a) Effect of time onto percent swelling of Psy-cl-poly(AAm) in different oil-water emulsions. (b) Effect of temperature on to percent swelling (P\-(s)) of Psy-cl-poly(AAm) in different oil-water emulsions.

Temperature of the swelling media is varied from 25 to 50°C and it has been observed that temperature variation showed a marked effect on P_s of the hydrogel. P_s increases with increase in temperature up to 45°C and desorption starts with further increase in temperature for all the oil-water emulsions (Fig. 9b). It can be explained on the basis that with increase in temperature, the absorbent becomes more compact and leads to desorption of the absorbed solvent. Thus Psy-cl-poly(AAm) gels are temperature sensitive smart polymers. It is found that the gel (100 mg) at optimum temperature can remove 6.9, 6.85, 7.55 and 7.1% of water from petrol-water, diesel-water, kerosene-water and petroleum ether-water emulsions, respectively (Table-1).

Effect of pH onto percent swelling

Water up-take capacity of the polymer is also investigated at different pH media (0.5N NaOH, distilled water and 0.5N HCl). It has been found that polymer gets disintegrated both in alkaline and acidic media but shows appreciable P_s in distilled water-oil emulsions. Since Psy-cl-poly(AAm) gels are not stable towards both acidic and basic media, the network structure of the absorbent starts breaking and ultimately disintegrate. This shows that Psy-cl-poly(AAm) gels are highly pH sensitive. At neutral pH, 6.9, 6.85, 7.55 and 7.1% of water removal is observed with 100 mg of sample from petrol-water, diesel-water, kerosene-water and petroleum ether-water emulsions, respectively (Table-1).

Effect of [NaCl] onto percent swelling

NaCl solutions of different concentrations (1 to 15%) were made and their emulsions were prepared with different oil samples in 1:1 ratio (80 ml). Known weights of the dried samples of the superabsorbent were put in to these emulsions for water uptake studies. It has been found that as the concentration of solution goes on increasing the superabsorbent shows an increase in P_s up to 10% but on further increase in NaCl concentration, a decrease in P_s has been observed (Fig. 10). It is due to the fact that after ionization of Na^+Cl^-, Na^+-ions enter inside the porous structure of the gel and being hydrophilic in nature causes more solvent to enter the gel structure thereby resulting in salt resistant swelling with increase in salt concentration. However, further increase in salt concentration resulted in desorption due to reverse osmosis process. Moreover, the percent water removal with 1% NaCl concentration was observed to be 5.0, 5.87, 6.75 and 6.37% from petrol-water, diesel-water, kerosene-water and petroleum ether-water emulsions, respectively (Table-1).

Tab. 1. Percent water removal from different oil-water emulsions.

	Varied parameters		Percent water removal from different oil-water emulsions			
			Petrol-water	Diesel-water	Kerosene-water	Petroleum-water
Psy-cl-poly(AAm)	Time (h) (25℃)	04	2.40	2.57	4.37	4.40
		08	4.55	4.55	5.22	5.72
		12	5.90	5.02	6.70	6.75
		16	5.95	5.32	6.85	6.77
		24	5.92	6.10	7.15	6.82
	Temperature (℃) (24 h)	25	5.92	6.10	7.15	6.82
		30	5.27	5.52	6.67	6.92
		35	5.97	5.90	7.45	6.80
		40	6.0	6.40	7.47	6.97
		45	6.90	6.85	7.55	7.10
		50	7.10	5.80	5.27	6.85
	pH (45℃, 24 h)	4.0	-	-	-	-
		7.0	6.90	6.85	7.55	7.10
		9.0	3.2	-	-	-
	NaCl concentration (%) (45℃, 24 h, 7.0 pH)	01	5.0	5.87	6.75	6.37
		05	5.72	5.72	6.97	6.42
		10	5.87	6.07	7.0	6.87
		15	5.62	4.33	5.33	4.57

Where (–) means that the polymer was disintegrated

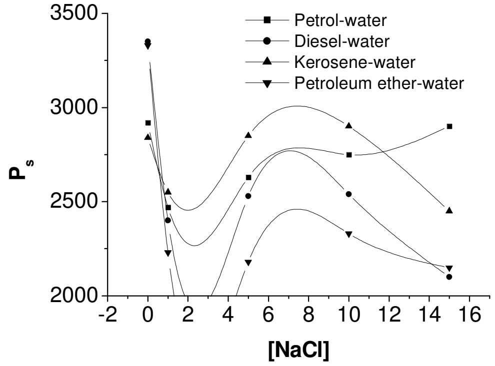


Fig. 10. Effect of NaCl concentration on to percent swelling (P\-(s)) of Psy-cl-poly(AAm) in different oil-water emulsions.

Experimental part

Materials and Method

Psyllium (AR, Sidhpur Sat-Isabgol Factory), Acrylamide (AR, LOBA, Chemie Pvt. Ltd.,), Potassium persulphate (AR, S. D. Fine) and Hexamethylene tetramine (AR, LOBA Chemie Pvt. Ltd.) were used as received.

FTIR spectra of the gels were recorded in KBr pellets using Perkin Elmer spectrophotometer, weighing was done on electronic balance (LIBROR AEG-220, Shimadzu). SEM of the samples was taken on Jeol Steroscan 150 Microscope and TGA/DTA studies were carried-out on Leinesis thermal analyzer.

Synthesis of Psy-g-poly(AAm)

Acrylamide was grafted onto *Psyllium* (1.0g) using potassium persulphate as an initiator in vacuum (650mmHg). Initially reaction conditions were optimized by varying various reaction parameters such as initiator concentration, amount of water, vacuum, pH, reaction time and reaction temperature so as to get the optimized graft copolymer (Figs. 2a-2f). The percent grafting (P_g) was calculated as per the method reported earlier [20].

Synthesis of Psy-cl-poly(AAm)

Psy-g-poly(AAm) obtained was crosslinked with hexamethylene tetramine in vacuum (650mmHg). Optimization was carried-out with respect to maximum water absorption by varying the concentrations of monomer and crosslinker. The hydrogel with maximum swelling was taken to be as optimized hydrogel and was used for further studies (Figs. 6a-6b).

Water uptake studies in oil-water emulsions

Different oil-water emulsions (petrol-water, diesel-water, kerosene-water and petroleum ether-water) were prepared by mixing oil and water in 1:1 ratio (80 ml) and the mixtures were stirred vigorously over magnetic stirrers for about 10 minutes. The oil-water emulsions were then transferred to automatic Rotary shaker so as to maintain the emulsion conditions. 100 mg of each sample of Psy-cl-poly (AAm) was immersed in different oil-water emulsions and swelling was measured as a function of time, temperature, pH and NaCl concentration. In case of time factor swelling was taken at different time intervals (4, 8, 12, 16 and 24 h) and optimum swelling time was recorded. Afterwards, the samples were subjected to swelling at different temperatures (25, 30, 35, 40, 45 and 50°C) so as to find-out the optimum temperature for maximum swelling. This was followed by variation of pH (0.5N HCl, distilled water, 0.5N NaOH) and NaCl concentration (1, 5, 10 and 15%) at optimum time and temperature. The percent swelling (P_s) was calculated using method reported earlier [21].

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