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Synthesis of partially hydrolyzed graft copolymer (H-Ipomoea hederacea seed gum-g-polyacrylonitrile)

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ABSTRACT

Polyacrylonitrile was grafted to Ipomoea hederacea (Ih) seed gum with 138.5% grafting yield and 43.55% grafting efficiency in a procedure that was performed under homogeneous microwave (MW) irradiation conditions for 70 s in the absence of a radical initiator. Under similar conditions, a maximum grafting yield of 108% and 33.96% efficiency was achieved when the $K_2S_2O_8$/ascorbic acid redox system was used as a radical initiator in a thermostatic water bath at 35 °C. The effects of reaction variables, such as monomer/Ih seed gum concentration, MW power, and exposure time on the graft copolymerization were studied. The partially hydrolyzed graft copolymer (H-Ih-g-PAN) formed a loose, porous surface and improved the water absorbency of Ih seed gum. The swelling behavior of H-Ih-g-PAN in various ionic salt (NaCl, $MgCl_2$ and Na_2SO_4) solutions was also systematically investigated. The graft copolymer was further characterized using FTIR, TGA, XRD, and SEM.

1. Introduction

Loosely crosslinked hydrophilic polymers (hydrogels) are known as superabsorbants and are able to absorb and retain hundreds of times their weight in water. These superabsorbants are primarily used in sanitary goods to absorb bodily fluids, and in agriculture and horticulture to improve the water retention capabilities of soil (Po, 1994). Hydrogels are also valuable for specialized applications, such as the controlled delivery of bioactive agents. The first superabsorbent polymer (SAP), hydrolyzed starch-g-polyacrylonitrile (HSPAN), was developed by the U.S. Department of Agriculture at the Northern Regional Research Center in the late 1960s (Weaver et al., 1976); HSPAN has the ability to retain large amounts of water, saline, or biological fluid without dissolving (Buchholz & Graham, 1997). Since then, a variety of starches (Athawale & Rathi, 1999) and other polysaccharides, such as cellulose (Deo & Gotmare, 1999), carboxymethyl cellulose (Sand, Yadav, & Behari, 2010), hydroxyethyl cellulose (Miyata, Yokoyama, & Sakata, 1995; Salamone et al., 1985), sodium alginate (Kim, Yoon, & Ko, 2000; Yadav & Rhee, 2012) and partially carboxymethylated guar gum (Yadav, Sand, Mishra, & Behari, 2010) have been graft copolymerized into water-absorbing polymers. Polyacrylonitrile (PAN), polyacrylamide, and poly (acrylic acid) (Athawale & Lele, 2001) have frequently been grafted to starches using a variety of initiators, particularly the ceric saccharide redox system (Sugahara & Ohta, 2001). Attempts have been made to synthesize a new type of graft copolymer, Ipomoea hederacea (Ih) seed gum-g-PAN. Seed gums from Ipomoea plants are reported to be nonionic (Singh, Srivastava, Pandey, Sethi, & Sanghi, 2003), branched-chain polymers consisting of straight chains of mannose units joined by β-D (1 → 4) linkages with either α-D-galactopyranosyl units as side chains like guar gum or galactobiosyl units attached to the linear chain by α (1 → 6) linkages, as shown in Scheme 1. The galactose-to-mannose ratio and degree of branching varies by species and is 1:3 in Ih (Singh & Gupta, 2000). The seed gum of Ih (commonly known as Kaladana), which was selected for modification in this study, is widely distributed in India (Kirtikar, Basu, & An, 1975), is cultivated and can be found in the wild up to 6000 ft in the Himalayas. Ih is believed to be of American origin and can be found in all of the tropical and subtropical regions of the world. The seeds are reported to be highly medicinal and have laxative, purgative, anthelmintic, and carminative effects that are used to treat ailments, such as inflammations, abdominal diseases, fevers, headache, and bronchitis. Concurrent homopolymer formation is a major constraint in graft copolymerization and leads to low grafting yield. The use of microwave irradiation as an efficient source of thermal energy is becoming the standard technique in various fields of chemistry (Galema, 1997). This paper describes the synthesis of a graft copolymer (Ih-g-PAN) with 138.5% grafting yield and 43.55% grafting efficiency in a very short period, without the use of an inhibitor through the use of microwaves. Alternatively, $K_2S_2O_8$/ascorbic acid acting as a redox initiator in a thermostatic water bath at 35 ± 0.2 °C for one hour only achieved a 108% grafting yield and 33.96% grafting efficiency. The optimally synthesized

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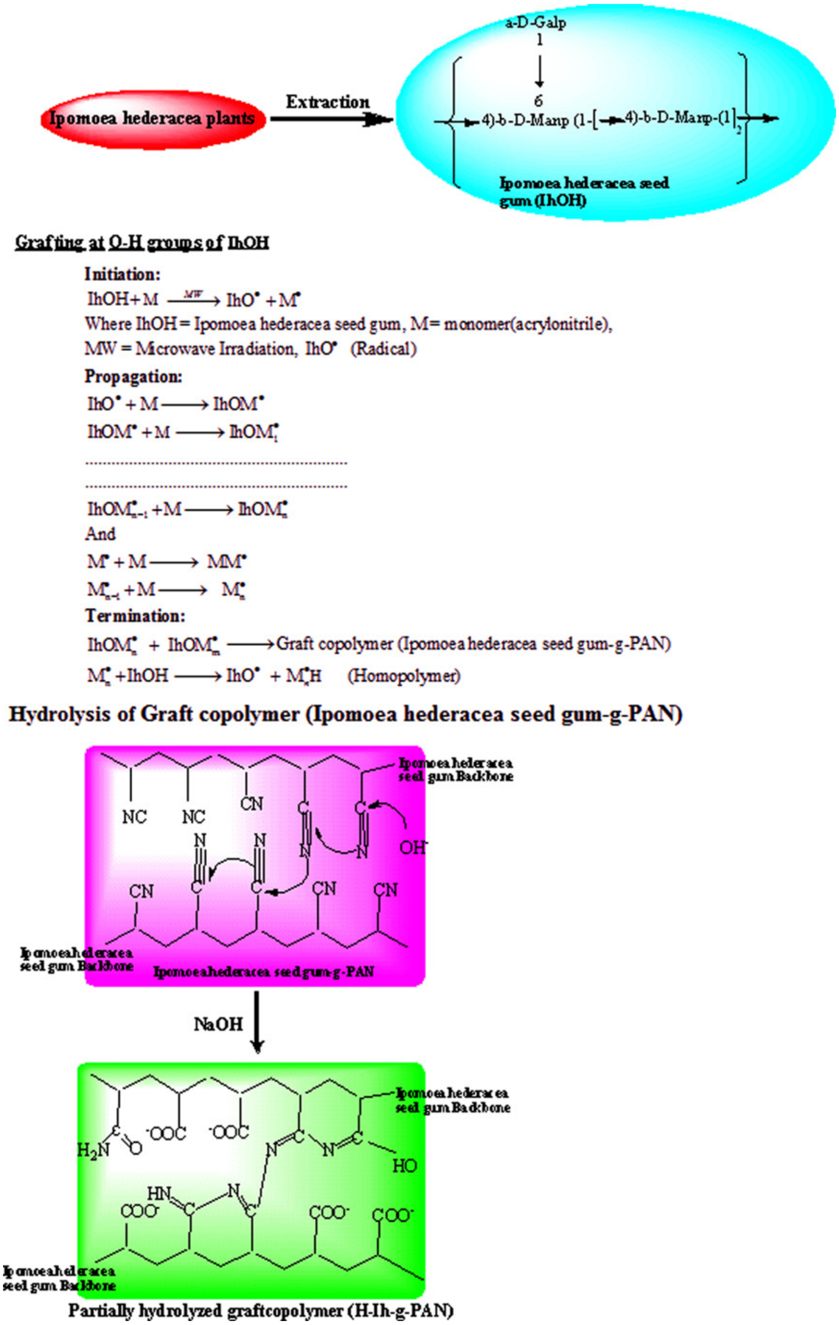

Scheme 1. Proposed mechanistic pathway for synthesis of partially hydrolysed graft copolymer (H-Ih-g-PAN).

graft copolymer (Ih-g-PAN) was then characterized and hydrolyzed in an alkaline medium to form a hydrogel hybrid network with super swelling characteristics.

2. Experimental

2.1. Materials

Seeds of Ih were supplied by Himani Seed Stores, Deheradun, India. Acrylonitrile (AN, Sigma Aldrich), $K_2S_2O_8$ (KPS, Sigma Aldrich), dimethylformamide (DMF, Merck), ascorbic acid (Sigma Aldrich), magnesium chloride (Sigma Aldrich), sodium chloride (Sigma Aldrich), and sodium sulfate (Sigma Aldrich) were of analytical grade and used as received. An unmodified Kenstar domestic microwave oven, model-OM-34 ECR, was used for the adsorbent synthesis. Methanol was provided by Daejung Reagent Chemicals Co. Ltd. (South Korea). Deionized water was used for the hydrogel preparation and swelling measurements.

2.2. Isolation and purification of Ipomoea hederacea seed gum

Ih seeds (1 kg) were extracted with light petroleum, followed by EtOH to remove fatty and coloring materials, and then suspended in 1% aqueous acetic acid overnight. The filtrate of the 1% solution was precipitated three times with 95% EtOH to produce a white amorphous product. The crude gum was then collected, washed with ethanol, and dried. The pure seed gum was a non-reducing, white, fibrous material.

2.2.1. Grafting under microwave irradiation in an aqueous medium

Calculated amounts of the Ipomoea hederacea seed gum (0.10 g/25 mL) and acrylonitrile (AN) (24×10^{-2} mol/L) were placed in 150 mL open necked flasks and irradiated in a domestic microwave oven at set microwave powers (20–100%)for different periods of time (20–80 s). The different graft samples of Ipomoea hederacea seed gum-g-poly(acrylonitrile) were separated from their respective reaction mixtures by the addition of excess amounts of DMF. The grafted samples were extracted with DMF in a Soxhlet apparatus for 4 h to dissolve all of the homopolymer. The colorless, grafted copolymer samples (Ih-g-PAN) were then dried under vacuum at 50 °C for over 24 h at a constant weight and the results were recorded. At an optimal microwave power and exposure time, the concentrations of the acrylonitrile and Ih were then varied to determine the best synthesis conditions.

2.2.2. Grafting using a $K_2S_2O_8$/ascorbic acid redox pair under a thermostatic water bath

Acrylonitrile (24×10^{-2} M) and ascorbic acid (2.1×10^{-2} M) were added to an aqueous solution of Ih seed gum (100 mg/25 mL) in a 150 mL reaction flask and thermostated in a water bath at 35 °C. After 30 min, $K_2S_2O_8$ (10×10^{-2} M) was added, with the time at addition taken as zero. Graft copolymerization was allowed for 1 h. The reaction product was then precipitated in DMF as previously described and the grafting ratio (%G) and efficiency (%E) were calculated as 108% and 33.96%, respectively.

2.2.3. Preparation of partially hydrolyzed graft copolymer (H-Ih-g-PAN)

Scheme 1 represents the general procedure for the preparation of the hydrolysis product. The Ih-g-PAN was saponified using a 10 mL aqueous sodium hydroxide (1 N) solution. In a loosely stoppered 100-mL flask, 0.45 g of the Ih-g-PAN powder was dispersed and gently stirred in the base solution at room temperature under atmospheric conditions for 5 min. The dispersion was then heated at 45 °C and magnetically stirred. The saponification was continued until the color of the mixture changed from deep orange-red to light yellow. The discoloration time was dependent on the base concentration and varied from 15 to 45 min. The pasty mixture was allowed to cool to room temperature and neutralized to pH 7.0 by the addition of a 10 wt% aqueous acetic acid solution. Methanol (200 mL) was added to the gelled product while stirring. After a few minutes, the Ih-g-PAN light yellow precipitate was filtered, washed with fresh methanol (200 mL), and dried overnight at 50 °C, resulting in the partially hydrolyzed graft copolymer (H-Ih-g-PAN).

2.2.4. Characterization methods

Wide-angle X-ray diffraction patterns of Ih, Ih-g-PAN, and H-Ih-g-PAN were recorded using a Rigaku Rotaflex (RU-200B) X-ray diffractometer employing Cu KR radiation with a Ni filter. The tube current was 300 mA with a tube voltage of 40 kV. The 2θ angular regions between 0° and 85° were explored. The FTIR spectra of Ih, Ih-g-PAN, and H-Ih-g-PAN were measured using a JASCO FT-IR spectrometer with KBr pellets ranging from 450 to 4000 cm^{-1}. ^1H spectra of Ih and Ih-g-PAN were recorded on JEOL 300 MHz FT NMR in D_2O. The surface morphologies of Ih, Ih-g-PAN, and H-Ih-g-PAN were studied by a field emission scanning electron microscope (FE-SEM) (LEO SUPRA 55, Carl Zeiss, Germany) at an acceleration voltage of 20 kV. The thermal stability of Ih, Ih-g-PAN, and H-Ih-g-PAN were investigated using a TA instrument (SDT Q600 V20.5 Build 15) analyzer from 50 °C to 900 °C under a nitrogen atmosphere at a heating rate of 10 °C.

2.3. Property investigation

2.3.1. Estimation of grafting parameters

The graft copolymer has been characterized as reported in the literature (Athawale & Lele, 1998).

2.3.2. Study of water absorbency of partially hydrolyzed graft copolymer (H-Ih-g-PAN)

The water absorbency of partially hydrolyzed graft copolymer in terms of swelling ratio (S_r) and percent swelling (P_s) has been calculated by using some reported work (Abd EL-Rehim, Hegazy EL-Sayed, & Ali, 2000).

2.3.3. Swelling in salt solutions

The water absorbent capacity of the partially hydrolyzed graft copolymer was determined in various saline solutions (NaCl, $MgCl_2$, and Na_2SO_4) of different concentrations according to the method described in Section 2.3.2.

2.3.4. Determination of swelling kinetics

A series of dried samples (0.05 g) were placed in excess distilled water. The superabsorbent materials were then separated from the unabsorbed water and weighed at set intervals. This process was repeated until the weight of the superabsorbents remained constant. The water absorbency at different times was then calculated according to Section 2.3.2.

3. Results and discussion

3.1. Determination of optimum reaction conditions

The copolymerization reaction for the graft copolymer (Ih-g-PAN) was performed with different monomer/Ih seed gum concentrations, MW power, and exposure times to study their effects on water absorbency.

3.2. Optimization of the grafting condition

3.2.1. Effect of microwave power and exposure time

Increasing the microwave power from 20% to 80% (240–1200 W) increased the grafting ratio and efficiency at a fixed concentration of acrylonitrile (0.24 M), Ih (0.1 g), exposure time (70 s), and reaction volume (25 mL). Increases in %G and %E with increasing microwave power may be due to the formation of more polysaccharide and acrylonitrile free radicals, resulting in more graft copolymerization. Microwave powers greater than 80% reduced the %G and %E, likely due to the degradation of polysaccharides and homopolymers (Table 1). Grafting increased with increases in exposure time, and was greatest was observed at a 70 s exposures at a fixed concentration of acrylonitrile (0.24 M), Ih (0.1 g), microwave power (80% or 1200 W), and reaction volume (25 mL). Gains in the grafting ratio and efficiency resulted from the availability of more microwave energy that generated more polysaccharide and acrylonitrile radicals for graft copolymerization (Table 1). However, prolonged exposure times led to the degradation of the grafting product occurred due to the high temperatures caused by the microwave energy.

3.2.2. Effect of monomer concentration

The effects of acrylonitrile (AN) concentration on graft copolymerization were studied by varying its concentration from 16×10^{-2} mol/L to 32×10^{-2} mol/L and fixing the other parameters (Ih = 0.1 g/25 mL, microwave power = 1200 W or 80%, exposure time = 70 s, reaction volume = 25 mL). The grafting parameters increased from 83.75% to 138.5% after increasing the AN concentration from 16×10^{-2} mol/L to 24×10^{-2} mol/L. This increase can

Table 1
Effect of microwave power and exposure time on grafting: [Ih] = 0.10 g/25 mL, [acrylonitrile] = 24 × 10^{-2} mol/L, reaction volume = 25 mL, microwave power = 80%, exposure time = 70 s.

S. no.	Microwave power	Exposure time (s)	Yield (g)	% G	%E	%H
1.	20	20	122.75	22.75	7.15	92.85
		40	134.68	34.68	10.90	89.10
		60	147.58	47.58	14.90	85.10
		70	161.94	61.94	19.40	80.60
		80	167.23	67.23	21.10	78.90
2.	40	20	157.35	57.35	18.10	81.90
		40	169.76	69.76	21.90	78.10
		60	183.59	83.59	26.30	73.70
		70	197.62	97.62	30.70	69.30
		80	189.50	89.50	28.10	71.90
3.	60	20	191.70	91.70	28.80	71.20
		40	203.50	103.50	32.50	67.50
		60	218.55	118.50	37.30	62.70
		70	228.30	128.30	40.40	59.60
		80	220.50	120.50	37.90	62.10
4.	80	20	196.75	96.75	30.40	69.60
		40	218.43	118.40	37.20	62.80
		60	227.60	127.60	40.10	59.90
		70	238.50	138.50	43.50	56.50
		80	226.50	126.50	39.80	60.20
5.	100	20	214.70	114.70	36.10	63.90
		40	202.50	102.50	32.20	67.80
		60	187.80	87.80	27.60	72.40
		70	163.50	63.50	19.90	80.10
		80	156.30	56.30	17.70	82.30

be explained by the greater availability of monomer molecules in close proximity to form the polymeric backbone. The monomer molecules, which are in the immediate vicinity of reaction sites become acceptors of Ih macro radicals (Ih•), resulting in chain initiation and thereafter becoming free radical donors to neighboring molecules leading to termination reduction. Beyond AN concentrations of 24 × 10^{-2} mol/L, grafting parameters decreased from 138.5% to 121.6%, which may be attributed to the increased viscosity of the reaction medium due to the formation of more homopolymers.

3.2.3. Effect of Ih seed gum concentration

The effects of Ih seed gum concentrations ranging from 0.05 to 0.25 g/25 mL on graft polymerization were studied at a fixed concentration of AN (24 × 10^{-2} mol/L), microwave power (1200 W), exposure time (70 s), and reaction volume (25 mL). Increasing the concentration of Ih resulted in the grafting ratio increasing from 97.40% to 138.50%, which may be due to the greater availability of grafting sites on Ih. Beyond Ih concentrations of 0.10 g/25, %G decreased from 138.50% to 112.8% and %E decreased from 43.50% to 35.40%. These reductions in grafting parameters may be due to the relative decrease in the concentration of the AN monomer and the increase in the viscosity of the reaction medium, thus hindering the rate of the desired reaction.

3.3. Determination of optimal reaction conditions

PAN can be successfully grafted with good yield using both a potassium persulfate/ascorbic redox initiator and microwave irradiation. However, with the same concentration of monomer, %G was greater in the microwave-synthesized copolymer sample due to incorporation of more PAN grafts. The optimal %G was obtained with 0.1 g seed gum exposed to 80% microwave power for 70 s in 24 × 10^{-2} M AN for a total volume of 25 mL. The copolymerization reaction for H-Ih-g-PAN was performed with different concentrations of precursors to study their effects on water absorbency. The representative samples of Ih-g-PAN, H-Ih-g-PAN, and crude Ih seed gum were characterized using FTIR, NMR, XRD, TGA, and SEM.

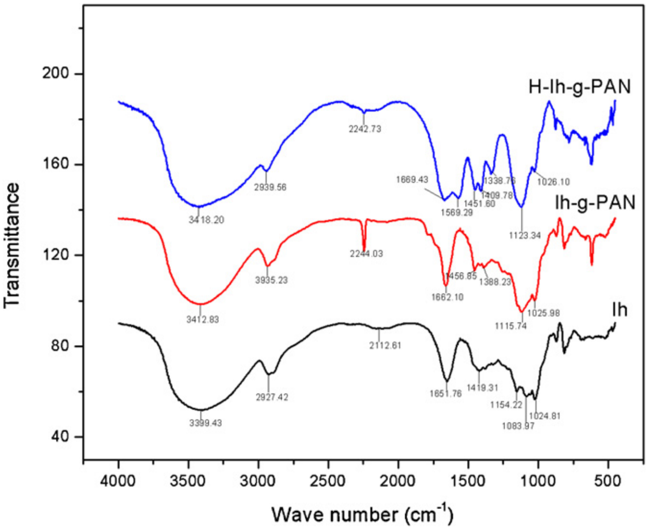

Fig. 1. FTIR of Ipomoea hederacea (Ih) seed gum, graft copolymer (Ih-g-PAN) and partially hydrolyzed graft copolymer (H-Ih-g-PAN).

3.4. Characterization of the partially hydrolyzed graft copolymer (H-Ih-g-PAN)

3.4.1. Fourier transform infrared spectroscopy

The IR spectrum of pure Ih gum has a broad, strong band at 3399.43 cm^{-1} due to O—H stretching, and a band at 2927.42 cm^{-1} due to C—H linkages, while the IR spectrum of Ih-g-PAN had a-O—H stretching peak at 3412.83 cm^{-1} An additional absorption peak at 2244.03 cm^{-1} (—CN group) was observed (Fig. 1), providing evidence of AN grafting to Ih. In addition, after the alkaline hydrolysis of the graft copolymer (Ih-g-PAN), new absorption modes were observed at 1669.43 cm^{-1} and 1409.78 cm^{-1} due to $>\mathrm{C{=}O}$ stretching and OH bending vibrations of the carboxylic groups, respectively.

3.4.2. ^{1}H NMR spectroscopy

^{1}H NMR of the pure seed gums showed a peak at δ 4.65 ppm for anomeric hydrogens and at δ 3.4–3.9 ppm due to sugar protons, whereas the grafted gums, besides the above peaks, also showed additional peaks at δ 2.05–2.06 ppm in Ih-g-PAN (due to $-\mathrm{CH_2}$ and —CH— protons at grafted PAN chains) indicating the grafting of PAN chains on to the Ipomoea hederacea gum molecules, whereas the number of peaks decreased in the δ 3.5–3.9 ppm region showing grafting at some of these sites (Fig. 2).

3.4.3. X-ray diffraction analysis

Fig. 3 exhibits the XRD patterns of Ih, partially hydrolyzed graft copolymer (H-Ih-g-PAN), and graft copolymer (Ih-g-PAN). XRD patterns were collected from 0° to 85° (2θ) at 25 °C. To measure the relative crystallinity (X_c) of the copolymer, the amorphous areas and crystalline peak areas were measured, and X_c was calculated from the diffraction intensity data ($2\theta = 0$–$85°$) with the following equation (Tang et al., 2008):

$$X_c = \frac{100 \times A_c}{A_c + A_a} \qquad (1)$$

where A_c and A_a are the areas of the crystalline and amorphous regions, respectively. With the above formula, the crystallinity of Ih, graft copolymer (Ih-g-PAN) and partially hydrolyzed graft copolymer (H-Ih-g-PAN) was calculated as 12.87%, 55.58% and 12.04%,

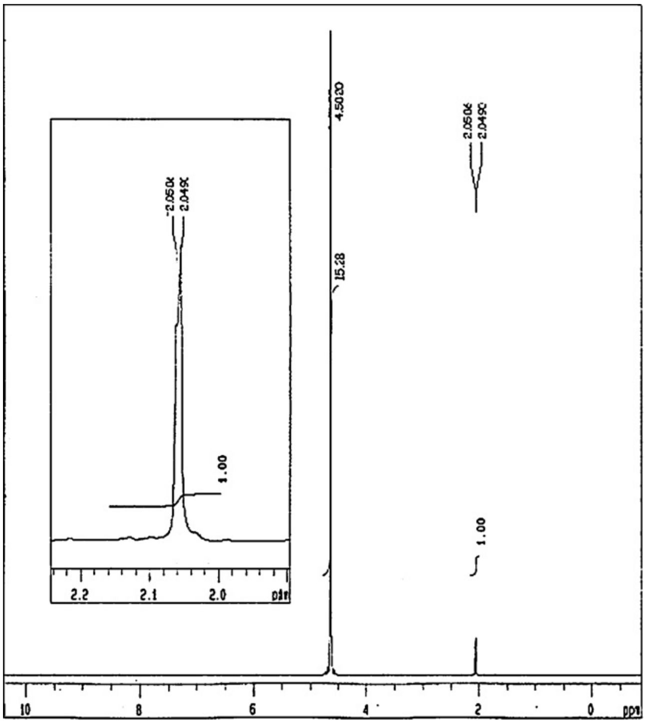

Fig. 2. NMR of Ipomoea hederacea seed gum and Ih-g-PAN.

respectively. X-ray diffraction spectra of the graft copolymer (Ih-g-PAN) show more crystalline areas (due to grafted polyacrylonitrile chains) than the Ih. X-ray diffraction studies illustrated that the crystallinity percentage of the graft copolymer decreased upon partial alkaline hydrolysis.

3.4.4. *Morphology analysis*

The SEM images of the Ih, graft copolymer (Ih-g-PAN), and partially hydrolyzed graft copolymer (H-Ih-g-PAN) are depicted in Fig. 4(a)–(c). The surface morphology of the H-Ih-g-PAN is obviously different from Ih and Ih-g-PAN. Ih and Ih-g-PAN display a smooth and tight surface, facilitating the permeation of water into the polymeric network. The pores of H-Ih-g-PAN are uniform because all pores have approximately same value. The obtained average sizes of pores were found 188.5 nm.

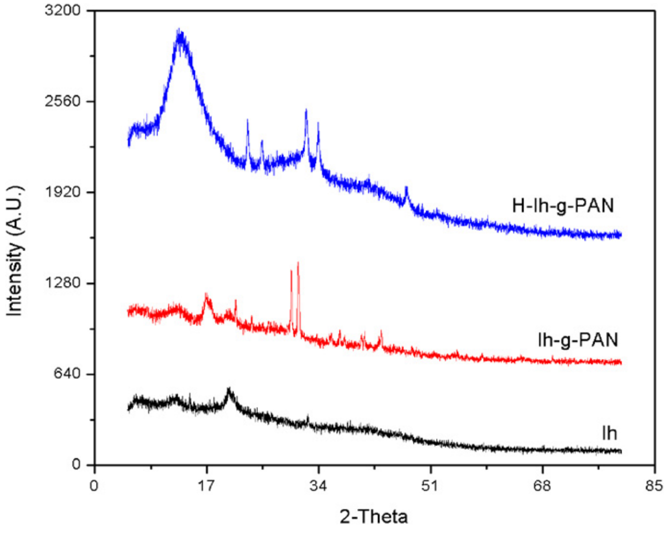

Fig. 3. XRD powder patterns of Ipomoea hederacea (Ih) seed gum, graft copolymer (Ih-g-PAN) and partially hydrolyzed graft copolymer (H-Ih-g-PAN).

3.4.5. *Thermogravimetric analysis*

The integral procedural decomposition temperature (IPDT) accounts for the whole shape of the thermogravimetric curve in a single number by measuring the area under the curve. Proposed by Doyle (1961), the IPDT has been correlated to volatile parts of polymeric materials and used for estimating the inherent thermal stability of polymeric materials (Vyazovkin & Sbirrazzuoli, 2006). IPDT was calculated using the following equations:

$$\text{IPDT}\quad (^{\circ}\text{C}) = A * K * (T_f - T_i) + T_i \tag{2}$$

$$A* = \frac{S_1 + S_2}{S_1 + S_2 + S_3} \tag{3}$$

$$K* = \frac{S_1 + S_2}{S_1} \tag{4}$$

where A^* is the area ratio of the total experimental curve defined by the total TGA thermogram, T_i is the initial experimental temperature, and T_f is the final experimental temperature. S_1, S_2, and S_3 values for calculating A^* and K^* are given in a reported work (Yadav, Sand, & Behari, 2012). The TGA curves of Ih, graft copolymer, and partially hydrolyzed graft copolymer are presented in Fig. 5(a)–(c), respectively, and show multi-step degradation. The 9.3% weight loss at 125 °C may be due to loss of absorbed water, which begins at approximately 74 °C. The polymer decomposition temperature (PDT) was found at approximately 280 °C. The rate of weight loss increases as the temperature increases from 75 °C to 300 °C and thereafter decreases to a maximum value of approximately 74.10% at 900 °C. The degradation of Ih occurs in one step between 200 and 400 °C. The T_{max} of 300 °C was due to this one-step degradation (in the DTG figure). In addition, the thermal stability of pure Ih and Ih-g-PAN can be determined by calculating IPDT values. IPDTs and the final decomposition temperatures (FDTs) of Ih were 928 °C and 800 °C, respectively. However, in the case of Ih-g-PAN, the 15% weight loss at approximately 254 °C may be due to the loss of absorbed water. The PDT was 254 °C with the degradation of Ih-g-PAN starting at approximately 150 °C (Fig. 5). The rate of weight loss increased as the temperature rose from 200°C to 400°C, and then decreased and attained a maximum of 67.89% at approximately 900 °C. The degradation of Ih-g-PAN occurred in multiple steps: 150–200 °C, 200–350 °C, 350–500 °C, and 600–800 °C. The T_{max} for these intervals were determined for the four-step degradation (in DTG figure). The DSC curve of Ih, Ih-g-PAN and H-Ih-g-PAN are also given in Fig. 5. The IPDT and FDT of Ih-g-PAN were 1155 °C and 900 °C, respectively. Comparison of the thermograms of Ih and Ih-g-PAN indicated the FDT and IPDTs were greater for Ih-g-PAN, indicating that Ih-g-PAN is more thermally stable than Ih. The degradation temperatures of H-Ih-g-PAN are listed in Fig. 5.

3.4.6. *Swelling kinetics of partially hydrolyzed graft copolymer (H-Ih-g-PAN)*

Swelling kinetics were characterized by the Voigt-based viscoelastic model (Kabiri, Omidian, Hashemi, & Zohuriaan-Mehr, 2003; Omidian, Hashemi, Sammes, & Meldrum, 1998):

$$S_t = P(1 - e^{-t/r}) \tag{5}$$

where S_t is the swelling capability at any moment (g/g), p is the power parameter (g/g), t is the time (min), and r is the rate parameter (time required to reach equilibrium swelling, min). The data obtained from the equilibrium swelling and swelling rate for each sample was fit to Eq. (5) to determine the rate and power parameters. The rate parameter, r, is a measure of the swelling rate of a superabsorbent sample, with a lower r-value indicating a faster

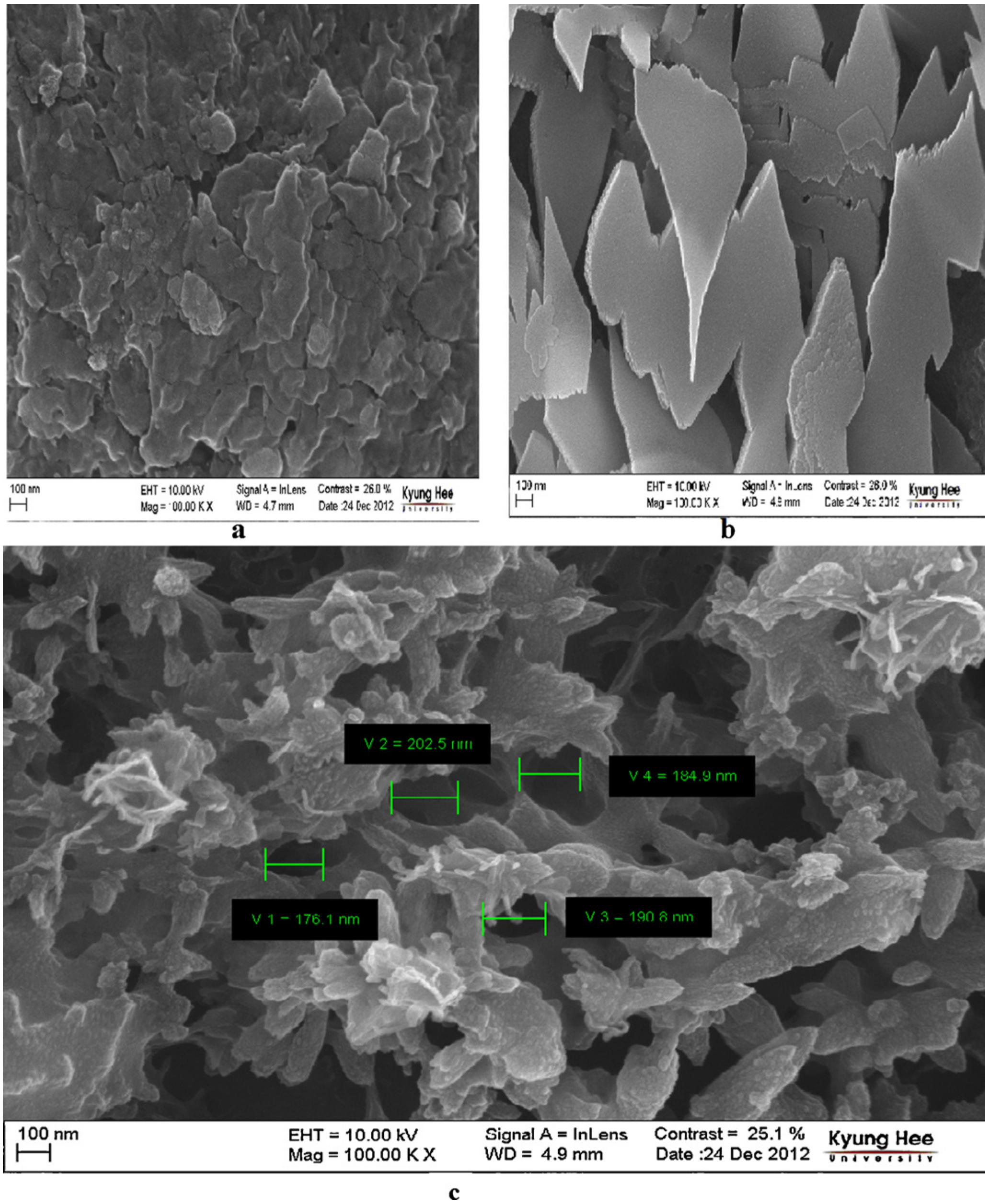

Fig. 4. SEM micrographs of (a) Ipomoea hederacea (Ih) seed gum (b) graft copolymer (Ih-g-PAN) and (c) partially hydrolyzed graft copolymer (H-Ih-g-PAN).

swelling rate. The power parameter, *p*, reflects the water-holding capacity of an individual superabsorbent. The swelling kinetics of a superabsorbent composite is shown in Fig. 6. The swelling rate of Ih is greatest within the first 300 min, and is then reduced later on. Alternatively, the swelling rate of H-Ih-g-PAN increased with time and attained its maximum value. The rate parameters for the Ih and H-Ih-g-PAN samples were 72.03 and 476.19 min, respectively. However, the *p*-value showed a different trend, with Ih and H-Ih-g-PAN values of 26.51 and 364.07 g/g, respectively. Though the *r*-value for H-Ih-g-PAN is greater than Ih, the *p*-value is much greater, suggesting that a partially hydrolyzed graft copolymer can provide greater water absorbency.

3.4.7. The swelling properties of the partially hydrolyzed graft copolymer (H-Ih-g-PAN)

The equilibrium swelling capacity of the H-Ih-g-PAN hydrolysis product was measured in distilled water and different saline solutions. The dimensionless salt sensitivity (f) (Zohuriaan-Mehr & Pourjavadi, 2003) was calculated according to Eq. (4):

$$f = \frac{1 - S_{\text{salt}}}{S_{\text{water}}} \tag{6}$$

where S_{salt} and S_{water} are the amount of swelling in a given saline solution and distilled water, respectively.

Table 2A exhibits the swelling data of the hydrolysis product. The hydrolysis product absorbed water at rates as high as

Table 2A
Swelling capacity (g/g) and dimensionless factor of salt sensitivity (f) for the partially hydrolyzed graft copolymer (H-Ih-g-PAN) in various swelling media.

Swelling medium	Swelling capacity (g/g)	f
Distilled water	146.32	–
0.1 wt% solution of NaCl	45.72	0.708
0.1 wt% solution of $MgCl_2$	17.72	0.879
0.1 wt% solution of Na_2SO_4	32.52	0.787

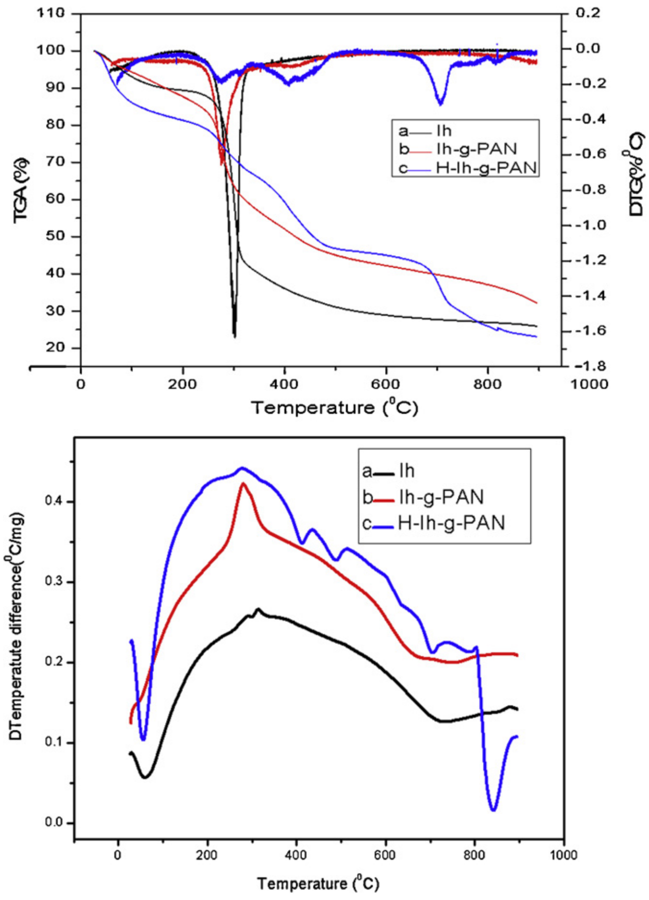

Fig. 5. TGA/DTG/DSC of (a) Ipomoea hederacea (Ih) seed gum, (b) graft copolymer (Ih-g-PAN) and (c) partially hydrolyzed graft copolymer (H-Ih-g-PAN).

146.32 g/g. Therefore, the product can be referred to as a superswelling or superabsorbent polymer (SAP) hydrogel. The swelling properties of H-Ih-g-PAN in different concentrations of NaCl, $MgCl_2$, and Na_2SO_4 solutions are shown in Table 2B. Based on the experimental results, the absorbency of H-Ih-g-PAN is very high for distilled water at lower salt concentrations (0.1 wt%). However, the swelling capacity of this hydrolysis product was significantly decreased with increasing concentrations of the salt solution. Water absorbency for H-Ih-g-PAN in the studied solutions varied based on the concentrations of monovalent and divalent cations, with water absorbency decreasing as the salt concentrations became more multivalent and less monovalent. The salt type and concentration can be expressed in terms of ionic strength (Bao, Ma, & Li, 2011):

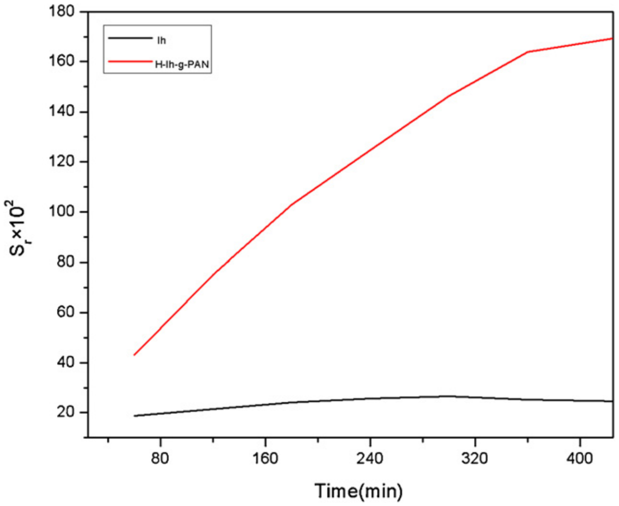

Fig. 6. The swelling kinetics of Ipomoea hederacea (Ih) seed gum and partially hydrolyzed graft copolymer (H-Ih-g-PAN).

Table 2B
Swelling behavior of composite in different salt solutions.

Wt% salt solution	Ionic strength (mol ion/dm³)			$P_s = S_r \times 10^2$		
	NaCl	$MgCl_2$	Na_2SO_4	NaCl	$MgCl_2$	Na_2SO_4
0.1	0.0171	0.015	0.021	4572	1772	3252
0.3	0.051	0.044	0.063	3432	1566	3018
0.5	0.086	0.074	0.105	3332	1698	2544
0.7	0.119	0.104	0.147	3120	1676	2334
0.9	0.154	0.133	0.189	2464	1660	2320
1.1	0.188	0.163	0.232	2450	1232	1970
1.3	0.222	0.193	0.274	1214	1226	1960
1.5	0.257	0.222	0.317	1205	1210	1945

$$\text{Ionic strength} \quad (I) = 0.5 \sum (C_i Z_i^2) \tag{7}$$

where I, C_i, and Z_i are the ionic strength, ionic concentration, and charge on each individual ion, respectively.

As shown in Table 2B, the order of the isotonic and non-isotonic salt solution of ionic strength is $Mg^{2+} > Na^+$ and $SO_4{}^{2-} > Cl^-$. The effect of the ionic strength on the water absorbency can be expressed by Flory's equation (Flory, 1953):

$$q_m^{5/3} = [(i/2\nu_u S_*{}^{1/2})^2 + (1/2 - X_1)/\nu_1]/\nu_e/V_0 \tag{8}$$

According to Section 2.3.2, when the ionic strength of a saline solution increases, the water absorbency decreases. Therefore, the experimental results abide by Flory's equation. The observed results can be explained as follows: in multi-valent cationic solutions, the complexes formed by hydrophilic groups and multi-valent cations result in 'ionic crosslinks' in the superabsorbent network, which cause an increase in the network density and reduced swelling capacity (Shi, Wang, & Wang, 2011). In terms of the swelling percentage, water absorbency decreased as the concentrations of the various salt solutions increased, which can be explained by the 'charge screening effect' in salt solutions. In addition, excess cations cause non-perfect, anion–anion electrostatic repulsion that decreases the osmotic pressure difference between the gel network and external solution, thereby drastically reducing swelling capacity (Murali Mohan, Keshava Murthy, & Mohana Raju, 2005). To investigate the effects of different anions on the water absorbency of H-Ih-g-PAN, samples were prepared with equal concentrations of NaCl and 1/2(Na_2SO_4) solution (i.e. the contribution of Na^+ to the whole ionic strength is equal, regardless of the valence of the anions). Table 2B shows the impact of Cl^- and $SO_4{}^{2-}$ on the saturated water absorbency of H-Ih-g-PAN, with the anion valence having an effect on the water absorbency of the superabsorbent. The water absorbencies of H-Ih-g-PAN were greater in solutions containing divalent anions ($SO_4{}^{2-}$) than those containing monovalent anions (Cl^-) at the same concentrations. Due to ionic crosslinking by multi-valent cations (Mg^{2+}), the salt sensitivity of the super swelling hydrogel in multi-valent solutions was greater than that of solutions containing univalent cations, such as Na^+.

4. Conclusion

In the present study, a graft copolymer (Ih-g-PAN) was efficiently synthesized without a radical initiator or catalyst in a very short reaction time of 70 s using MW irradiation. Furthermore, the grafting yield was greater in the MW than that with the redox initiator ($K_2S_2O_8$/ascorbic acid). Thus, grafting under MW offers an economical and quick method for Ih seed gum grafting. FTIR indicates that the graft-copolymerization reaction occurs between Ih seed gum and PAN. SEM studies illustrate the partially hydrolyzed graft copolymer (H-Ih-g-PAN) had a loose and porous surface, facilitating the permeation of water into the polymeric network. In addition, XRD analysis shows that crystallinity of the graft copolymer decreased upon partial alkaline hydrolysis. TGA implied that the introduction of PAN into the ID seed gum leads to an increase in thermal stability of the partially hydrolyzed graft copolymer (H-Ih-g-PAN). The impact of salts on water absorbency of H-Ih-g-PAN is relative to the concentration of salt solution and valence of cations. The swelling-loss behavior of the hydrogel occurred as the concentration of the external salt solution increased. The effect of various cationic salt solutions (NaCl and $MgCl_2$) and anionic salt solutions (NaCl and Na_2SO_4) on the swelling has the following order: $Na^+ > Mg^{2+}$, $Cl^- > SO_4^{2-}$. The water absorbency of the hydrolysis product increased and then decreased. The swollen gel strength of the hydrolysis product improved due to the loose and porous surface.

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