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Synthesis, characterization and applications of polymethylmethacrylate grafted psyllium as flocculant

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ABSTRACT

Polymethylmethacrylate grafted psyllium (Psy-g-PMMA) was synthesized by microwave assisted method. The grafting of the PMMA chains on the psyllium backbone was confirmed through the study of intrinsic viscosity, FTIR spectroscopy, elemental analysis, SEM and number average molecular weight ($\overline{M}n$). The intrinsic viscosity and number average molecular weight ($\overline{M}n$) of psyllium appreciably improved on grafting of PMMA chains. Further, flocculation efficacy of the graft copolymer was studied in kaolin suspension through *jar test* procedure, towards possible application as flocculant.

1. Introduction

Psyllium is derived from the seed of the *Plantago ovata* plant. It is also known as Ispaghula and Isabgol. Psyllium husk is a bulking fibre, after ingestion it expands and forms gelatin like mass in the colon by drawing in water. Once this occurs, the husks are able to "scrub" the intestines clean and transport waste through the intestinal tract. Several population based studies also suggest that increased fibre intake may reduce the risk of colon cancer (Petchetti, Frishman, Petrillo, & Raju, 2007; Rakel, 2007; Saper, Eisenberg, & Phillips, 2004; Sartore et al., 2009).

Psyllium husk is valued for its nutraceuticals, pharmaceuticals and medicinal applications. It is generally treated as a laxative, which possesses a plethora of health benefits and has proven to be effective in treating irritable bowel syndrome, constipation, diabetes, high cholesterol, obesity, colon cancer, ulcerative colitis and atherosclerosis among various other health conditions.

One of the most effective ways of modification of psyllium is by graft copolymerization with suitable monomers (Mishra, Rajani, Agarwal, & Dubey, 2002; Mishra, Srinivasan, & Gupta, 2003; Sen, Mishra, Usha Rani, Rani, & Prasad, 2012). The properties of the end product (grafted psyllium) can be suitably modulated in terms of percentage grafting. The end product macromolecule is thus programmed at the molecular level for desired applications.

The most contemporary technique in graft copolymerization involves the use of microwave radiations to initiate the grafting reactions. Superiority of this technique over others has been well discussed in earlier studies (Bharti, Mishra, & Sen, 2013; Mishra, Mukul, Sen, & Jha, 2011; Mishra, Rani, & Sen, 2012; Mishra & Sen, 2011; Mishra, Sen, Rani, & Sinha, 2011; Pal, Ghorai, Dash, Ghosh, & Udayabhanu, 2011; Pal, Sen, Ghosh, & Singh, 2012; Sen, Ghosh, Jha, & Pal, 2011Sen, Kumar, Ghosh, & Pal, 2009; Sen, Mishra, Jha, & Pal, 2010; Sen & Pal, 2009a,b; Sen, Singh, & Pal, 2010; Sinha, Mishra, & Sen, 2013; Usha Rani, Mishra, Sen, & Jha, 2012). Microwave based graft copolymer synthesis is further classified into two types: *microwave initiated* synthesis (using microwave radiation alone to initiate grafting) and *microwave assisted* synthesis (using a synergism of microwave radiation and chemical free radical initiator to initiate grafting).

The most profound change due to grafting takes place in branching of the macromolecule and in drastic increase in hydrodynamic volume – both of which are the selection criteria for a good flocculant (Brostow, Pal, & Singh, 2007; Singh, 1995; Singh et al., 2000).

The study described in this paper involves grafting of polymethylmethacrylate (PMMA) onto the backbone of psyllium, thus resulting in formation of polymethylmethacrylate grafted psyllium (Psy-g-PMMA). The synthesis has been carried out by *microwave assisted* method, which involves a synergism of microwave radiations and ceric ammonium nitrate (CAN) to initiate the grafting reaction. The flocculation efficacy of the grafted product has been studied in kaolin suspension by *Jar test* and *settling test* procedures.

2. Materials and methods

2.1. Materials

Psyllium husks were procured from Kamal & Sons, Sidhpur, India. Methyl methacrylate (99%) was purchased from CDH, India

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Table 1
Synthesis details of polymethylmethacrylate grafted psyllium (Psy-g-PMMA):.

Polymer grade	Wt. of psyllium (g)	Wt. of methylmethacrylate (g)	Wt. of CAN (g)	Time of irradiation (up to gel formation)	Percentage grafting (% G)	Number average molecular weight (kDa)	Intrinsic viscosity (dl/g)
Psy-g-PMMA 1	1	10	0.1	70 s	15.47	1923	1.16
Psy-g-PMMA 2	1	10	0.2	73 s	70.65	3661	1.45
Psy-g-PMMA 3	1	10	0.3	90 s	193.00	7650	4.36
Psy-g-PMMA 4	1	10	0.4	150 s	98.26	4662	2.09
Psy-g-PMMA 5	1	5	0.3	105 s	90.19	4311	1.92
Psy-g-PMMA 6	1	15	0.3	180 s	100.27	4914	2.23
Psyllium	–	–	–	–	–	1410	0.81

$\%\text{grafting} = \frac{\text{wt. of graft copolymer} - \text{wt. of polysaccharide}}{\text{wt. of polysaccharide}} \times 100.$

and acetone was purchased from Rankem, New Delhi, India. All the chemicals were used as received; without further purification.

2.2. Synthesis

2.2.1. Microwave assisted synthesis of polymethylmethacrylate grafted psyllium (Psy-g-PMMA), using ceric ammonium nitrate (CAN) as free radical initiator

1 g of psyllium was dissolved in 50 ml distilled water. Desired amount of methylmethacrylate was added to the psyllium solution amid high speed stirring, followed by addition of catalytic amount of ceric ammonium nitrate (CAN). They were mixed under high speed stirring (to affect a suspension of methylmethacrylate in the reaction mixture) and transferred to the microwave reactor (Catalyst^{TM} system CATA 4 R). In the reactor, stirring was continued and irradiated with microwave radiation (700 W) until gelling sets in, keeping the irradiation cut-off temperature at 70 degree centigrade. Once the microwave irradiation procedure got completed, the gel like mass left in the reaction vessel was cooled and poured into excess of acetone. The precipitated grafted polymer was collected and was dried in hot air oven. Subsequently, it was pulverized and sieved. The synthesis details of various grades of the graft copolymer have been shown in Table 1. The percentage grafting of this microwave assisted synthesized Psy-g-PMMA was evaluated as:

$$\%\text{grafting} = \frac{\text{wt. of graft copolymer} - \text{wt. of polysaccharide}}{\text{wt. of polysaccharide}} \times 100$$

The synthesis outline and proposed mechanism of synthesis has been depicted in Scheme 1(a) and (b) and the synthesis details of various grades of the graft copolymer have been shown in Table 1.

2.2.2. Purification of the graft copolymer by solvent extraction method

In an attempt to check possibility of any competing homopolmerization reaction, the whole synthesis process was repeated as above; but in the absence of the polysaccharide (psyllium), No product was obtained. This implies that the above process either does not involve any parallel homopolymerization reaction or even if any homopolymer happens to be formed, it cannot be precipitated under the given setup.

However as an added precaution, any occluded polymethylmethacrylate (PMMA) formed by competing homopolymerization reaction was removed by solvent extraction using acetone for 24 h (Kongparakul, Prasassarakich, & Rempel, 2008).

2.3. Characterization

2.3.1. Intrinsic viscosity measurement

Viscosity measurements of the polymer solutions were carried out with an Ubbelodhe viscometer (Constant: 0.003899) at 25 °C. The viscosities were measured in aqueous solutions at neutral pH. The time of flow for solutions was measured at four different concentrations (0.1%, 0.05%, 0.025% and 0.0125%). From the time of flow of polymer solutions (t) and that of the solvent (t_0, for distilled water), relative viscosity ($\eta_{rel} = t/t_0$) was obtained. Specific viscosity (η_{sp}), reduced viscosity (η_{red}) and inherent viscosity (η_{inh}) were mathematically calculated as:

$$\eta_{sp} = \eta_{rel} - 1$$

$$\eta_{red} = \frac{\eta_{sp}}{C}$$

$$\eta_{inh} = \ln \frac{\eta_{rel}}{C}$$

where 'C' represents polymer concentration in g/dl.

The reduced viscosity (η_{red}) and the inherent viscosity (η_{inh}) were simultaneously plotted against concentration. The intrinsic viscosity was obtained from the point of intersection after extrapolation of two plots (i.e. η_{red} versus C and η_{inh} versus C) to zero concentration (Collins, Bares, & Billmeyer, 1973). The intrinsic viscosity thus evaluated for various grades of the graft copolymer has been reported in Table 1.

2.3.2. Elemental analysis

The elemental analysis of psyllium and that of Psy-g-PMMA 3 (best grade) was carried out by an Elemental Analyser (Make – M/s Elementar, Germany; Model – Vario EL III). The estimation of four elements, i.e. carbon, hydrogen, nitrogen and oxygen were undertaken. The results have been summarized in Table 2.

2.3.3. FTIR spectroscopy

The FTIR spectra of psyllium and of Psy-g-PMMA 3 (Fig. 1) were recorded in solid state, by KBr pellet method, using a FTIR spectrophotometer (Model IR-Prestige 21, Shimadzu Corporation, Japan) between 400 and 4000 cm^{-1}.

2.3.4. Scanning electron microscopy

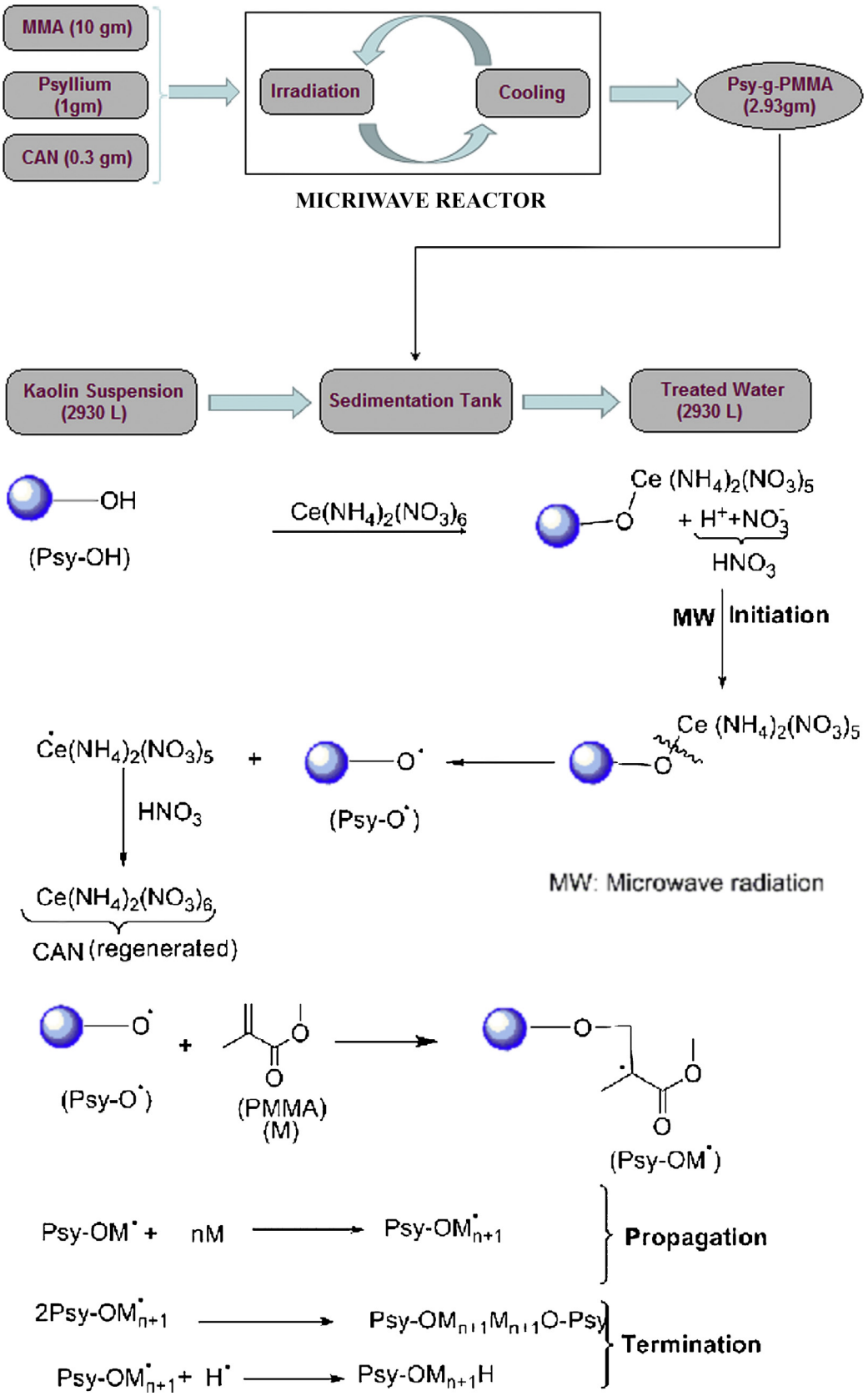
Surface morphology of psyllium (Fig. 2(a)) and Psy-g-PMMA 3 (Fig. 2(b)) were analysed in scanning electron microscopy (SEM) in powdered form (Model: JSM-6390LV, Jeol, Japan).

2.3.5. Determination of number average molecular weight ($\overline{M}n$)

The number average molecular weight of psyllium and various grades of Psy-g-PMMAs were determined in aqueous medium by Osmometry (A+ Adv. Instruments, INC. Model 3320, Osmometer). The correlation between number average molecular weight, intrinsic viscosity and percentage grafting has been depicted in Fig. 3.

Table 2
Elemental analysis.

Polymer grade	%C	%H	%O	%N
Psyllium	39.43	6.53	54.03	0.00
PMMA	60.06	8.03	31.90	0.00
Psy-g-PMMA 3	49.46	8.27	42.26	0.00



Scheme 1. (a) Synthesis outline for the formation of Psy-g-PMMA. (b) Schematic representation of mechanism for 'Microwave assisted synthesis of Psy-g-PMMA'.

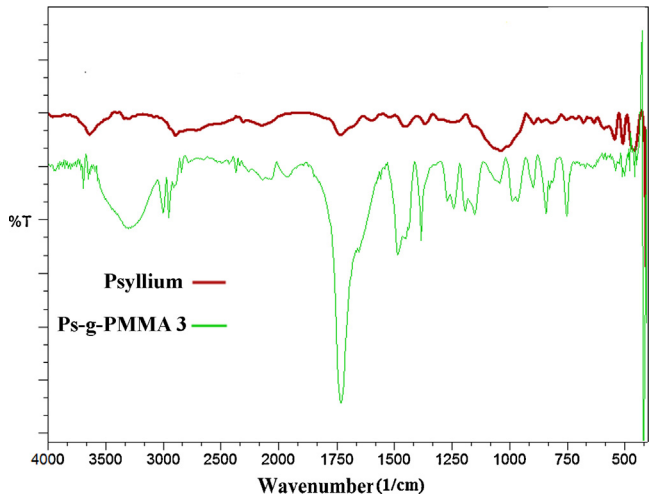


Fig. 1. FTIR spectra of psyllium and Psy-g-PMMA 3.

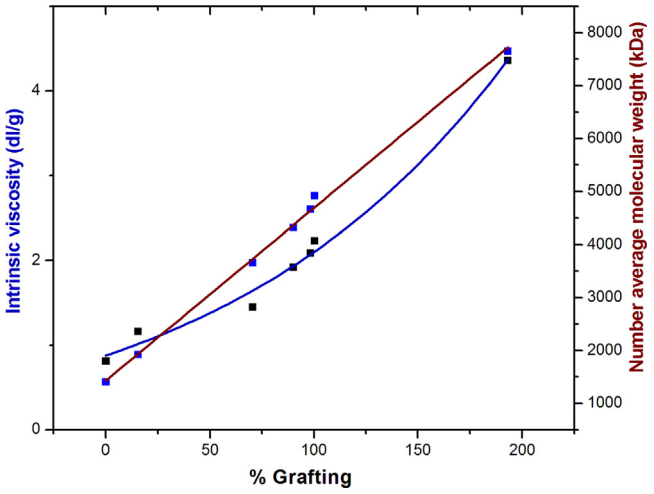


Fig. 3. Co-relation graph of intrinsic viscosity, percentage grafting and number average molecular weight of psyllium and different grades of Psy-g-PMMA.

2.4. Flocculation study in kaolin suspension

Flocculation efficacy of all the synthesized grades of Psy-g-PMMA, psyllium (starting material), polyacrylamide (commercial flocculant) and Alum (Coagulant) were studied by standard '*jar test*' procedure, in 0.25% kaolin suspension of average particle size ~130 nm (Light scattering spectrophotometer – Model Nano S manufactured by Malvern Inst., UK). All flocculation experiments were carried out in *jar test* apparatus (Make: Simeco, Kolkata, India). The test protocol (Mishra et al., 2011a) followed involved taking measured quantity (800 ml) of the 0.25% kaolin suspension in each of 6 identical 1 l borosil beakers. Calculated amount of Alum (Coagulant), polyacrylamide (commercial flocculant), psyllium (starting material) or various grades of Psy-g-PMMA (synthesized flocculant) was added in concentrated solution form to achieve the desired dosage (ranging from 0 ppm to 1.25 ppm with increment of 0.25 ppm, among the six beakers). The solutions were identically stirred (in *jar test* apparatus), at 150 rpm for 30 s, 60 rpm for 5 min, followed by 15 min of settling time. Afterwards, supernatant liquid was collected from each jar and turbidity was measured in a calibrated nephelo-turbidity meter (Digital Nephelo-Turbidity Meter 132, Systronics, India). Turbidity thus obtained was plotted against dosage for all grades of Psy-g-PMMA, psyllium, Polyacrylamide, and for Alum. The resulting flocculation profile has been reported in Fig. 4. The optimized dosage in each case is indicated by the *minima* of the curve.

Settling test employed a Stoppard graduated cylinder containing the 0.25% kaolin suspension (Sen & Pal, 2009a). The flocculant was added in concentrated solution form, to affect the optimized dosage (as determined by the *jar test* procedure above). The cylinder was mixed thoroughly by turning it upside down 10 times. Consequently, the cylinder was set upright, kept undisturbed and the height of the *clear water – suspension interface* tracked with respect

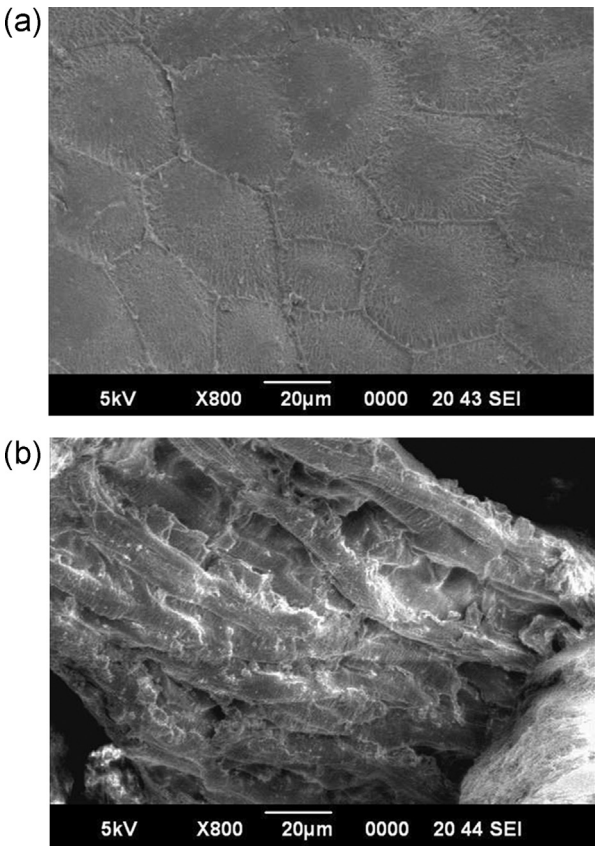


Fig. 2. SEM micrograph of (a) psyllium (b) Psy-g-PMMA 3.

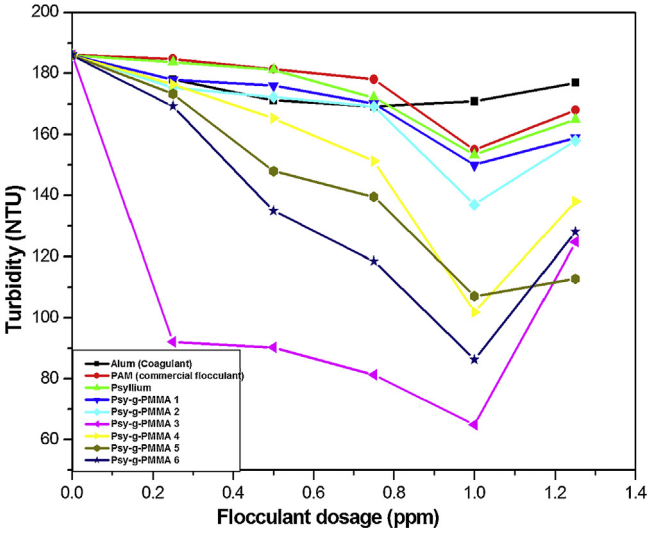


Fig. 4. Flocculation profile: Jar test in 0.25% kaolin suspension

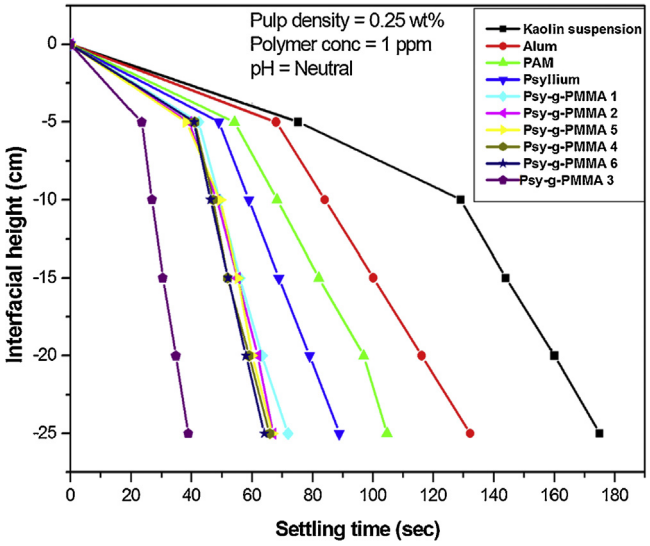


Fig. 5. Settling test in 0.25% kaolin suspension.

to time. The result is graphically plotted as *Interfacial height* vs. *settling time* plot (Fig. 5)

3. Results and discussion

3.1. Synthesis of Psy-g-PMMA by microwave assisted method

Psy-g-PMMA has been synthesized by microwave assisted method. The term *microwave assisted* has been coined by Mishra et al. in earlier studies (Mishra & Sen, 2011; Mishra et al., 2011a). It refers to a process of graft copolymer synthesis, which is a hybrid of microwave initiated and conventional method (chemical free radical initiator based method) of synthesis i.e. it is based on free radical mechanism using microwave radiation in synergism with chemical free radical initiator (ceric ammonium nitrate) to generate free radical sites on the polysaccharide (psyllium in this case) backbone. Various grades of the graft copolymer were synthesized by varying the ceric ammonium nitrate (CAN) and methylmethacrylate (monomer) concentration. In each case, the microwave irradiation of the reaction mixture was continued until it sets into a viscous gel like mass (or up to 3 min if no gelling took place), the microwave irradiation cutoff temperature being maintained at 70 degree centigrade throughout the process. The synthesis details have been tabulated in Table 1. The optimized grade has been determined through its higher percentage grafting, intrinsic viscosity and molecular weight. The approach of synthesis involved optimization with respect to CAN, keeping the methylmethacrylate concentration constant (i.e. Psy-g-PMMA 1, 2, 3, 4); followed by optimization with respect to methylmethacrylate, keeping the CAN concentration as optimized before (i.e. Psy-g-PMMA 3, 5, 6). From Table 1, it is obvious that the grafting is optimized at methylmethacrylate concentration of 10 g and CAN concentration of 0.3 g in the reaction mixture (50 ml), when the microwave power is maintained at 700 W (i.e. Psy-g-PMMA3).

CAN is electron deficient molecule, so it takes electrons from alcoholic oxygen in psyllium to form a new bond i.e. Ce—O. This bond being more polar (than O—H bond) breaks easily in the presence of microwave irradiation to form free radical site on the backbone of psyllium, from where the graft chains grow. The proposed mechanism of microwave assisted synthesis has been hypothesized in detail in earlier studies (Mishra & Sen, 2011; Mishra et al., 2011a; Rani, Sen, Mishra, & Jha, 2012). The proposed mechanism has been depicted in Scheme 1(b).

The synthesis outline has been depicted in Scheme 1(a).

3.2. Characterization

3.2.1. Estimation and interpretation of intrinsic viscosity

The intrinsic viscosity was evaluated for psyllium and the various grades of Psy-g-PMMA, as shown in Table 1. Intrinsic viscosity is practically the hydrodynamic volume of the macromolecule in solution (aqueous solution in this case). It is obvious from Table 1 that the intrinsic viscosities of all the grades of Psy-g-PMMA are greater than that of psyllium. Further, higher the percentage grafting, higher is the intrinsic viscosity. This can be explained by the increase in hydrodynamic volume due to the grafting of the PMMA chains on the main polymer backbone i.e. psyllium. The grafted PMMA chains increase hydrodynamic volume by two ways:

(1) By uncoiling of the polysaccharide chain through steric hindrance to intramolecular bonding.
(2) By contributing their own hydrodynamic volume.

Further, this is in good agreement with Mark–Houwink–Sakurada relationship (intrinsic viscosity $\eta = KM\alpha$ where K and α are constants, both related to stiffness of the polymer chains), applying which we can explain the increase in intrinsic viscosity as a result of increase in molecular weight (M) due to the grafted PMMA chains.

3.2.2. Elemental analysis

The results of elemental analysis for psyllium and that of the best grade of polymethylmethacrylate grafted psyllium (i.e., Psy-g-PMMA 3) are given in Table 2.

The elemental composition of Psy-g-PMMA 3 is intermediate of those of its constituents, as expected.

3.2.3. FTIR spectroscopy

From the FTIR spectrum of psyllium (Fig. 1), it has been observed that a small peak at 3631.96 cm^{-1} is due to stretching vibration of 1^0 —O—H (—CH_2OH). Smaller peak at 2889.37 cm^{-1} is assigned to the C—H stretching vibrations. The band at 1033.85 cm^{-1} is attributed to the C—O—C stretching vibrations.

In case of Psy-g-PMMA 3 (Fig. 1), we have additional peak due to the grafted PMMA chains. The peak at 1730.15 cm^{-1} is due to C=O stretching vibrations. This extra peak in case of Psy-g-PMMA is well explained by the presence of grafted PMMA chains and is confirmation of the intended grafting. The FTIR peaks of psyllium and that of Psy-g-PMMA are summarized in Supplementary Table 2.

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.carbpol.2013.08.047.

3.2.4. Scanning electron microscopy (SEM) analysis

It is evident from the SEM micrographs of psyllium (Fig. 2(a)) and that of the best grade of Psy-g-PMMA (Fig. 2(b)) that profound morphological change have taken place. The homogeneous structure of psyllium has been transformed to heterogeneous (fibrillar) structure. The homogenous morphology of psyllium is lost after grafting and transformed into heterogeneous (fibrillar) morphology.

3.2.5. Number average molecular weight of the polymers

As evident from Table 1, higher the percentage grafting, higher is the number average molecular weight. This is obvious due to the addition of more MMA monomers. The correlations have been depicted in Fig. 3.

3.3. Flocculation study

3.3.1. Flocculation study and dosage optimization in kaolin suspension

The flocculation study in 0.25% kaolin suspension (in *jar test* apparatus) for dosage from 0 ppm (control) to 1.25 ppm in increments of 0.25 ppm has been shown in Fig. 4. All the grades of grafted psyllium have shown better flocculation efficacy than the starting material (psyllium), polyacrylamide (commercial flocculant) and Alum (Coagulant). Further, higher the percentage grafting, higher is the flocculation efficacy. The higher flocculation efficacy of the grafted psyllium grades is due to their higher hydrodynamic volume (i.e. intrinsic viscosity) (Table 1). The higher hydrodynamic volume/higher radius of gyration of the macromolecule lead to higher flocculation efficacy in accordance with Brostow et al.'s model of flocculation. Thus, higher the percentage grafting, higher is the intrinsic viscosity. Higher the intrinsic viscosity, higher is the flocculation efficacy as reported in Supplementary Table 1. Evidently, among the various grades of Psy-g-PMMA, the grade with highest percentage grafting (Psy-g-PMMA 3) showed maximum flocculation efficacy. The better flocculation performance of the grafted psyllium than the raw material (psyllium) extends Singh's easy approachability model (Singh, 1995; Singh et al., 2000) which is for grafted PAM systems, to the realms of grafted PMMA systems.

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.carbpol.2013.08.047.

For all the grades of the graft copolymer, psyllium (starting material), commercial flocculant (PAM) and of alum studied, there is an optimal dosage at which the flocculation efficacy is maximum (i.e. the turbidity of the supernatant collected is minimum), beyond which the flocculation decreases (i.e. turbidity of the collected supernatant increases). This behavior of the flocculation curve finely confirms the *Bridging mechanism* (Ruehrwein & Ward, 1952). The optimal dosage of Psy-g-PMMA 3 as flocculant in 0.25% kaolin suspension is at 1 ppm.

The settling tests were carried out in 0.25 wt% kaolin suspension. In this case, the settling time was plotted against the height of interface. The flocculant dosage was maintained at 1 ppm (i.e. the optimized dosage as determined by *jar test* above). Fig. 5 shows the settling characteristics in kaolin suspension for alum, PAM, psyllium and different grades of Psy-g-PMMA. In complete agreement with the *jar test* above, Psy-g-PMMA 3 has the highest settling rate. Moreover, the settling rate of the various grades follow the same order as in *jar test* result (Fig. 4) i.e., higher the percentage grafting, higher is the settling rate. The settling rate is another reliable indicator of flocculation efficacy, having direct relation with radius of gyration (Brostow et al., 2007). The greater the settling rate of the floc containing contaminants, the greater will be its flocculation performance.

4. Conclusion

Polymethylmethacrylate grafted psyllium has been synthesized by *microwave assisted* method, using a synergism of microwave radiation and ceric ammonium nitrate (CAN) to initiate grafting reaction. The synthesized grades of the graft copolymer were characterized through various physicochemical techniques to ascertain the intended grafting. Further, the flocculation efficacy of various synthesized grades of the graft copolymer were studied through standard *Jar test* and *settling test* procedures in 0.25% kaolin suspension and were compared to that of the starting material (psyllium), commercial flocculant (PAM) and Coagulant (Alum). All the grafted psyllium grades have superior flocculation efficacy than others. Further, higher the percentage grafting, greater is the flocculation efficacy, in complete agreement with Brostow et al., model of flocculation.

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