



Photo-Induced Graft Copolymerization of Acrylonitrile onto Sodium Salt of Partially Carboxymethylated Psyllium

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ABSTRACT

Photo - induced grafting of acrylonitrile (AN) onto sodium salt of partially carboxymethylated psyllium (Na-PCMPsy) has been carried out using ceric ammonium nitrate (CAN) as a photo initiator in an aqueous medium. The reaction variables including concentrations of initiator, nitric acid, monomer and amount of the backbone as well as time and temperature have been varied for establishing grafting. The influence of these reactions conditions on the grafting yield has been discussed. The overall activation energy of grafting has been calculated. The FT-IR spectroscopy, thermal (TGA) and scanning electron microscopic (SEM) techniques have been used for the characterization of graft copolymer.

Key words: photo-grafting, ceric ammonium nitrate, optimized reaction conditions, activation energy, TGA

INTRODUCTION

Psyllium (Psy) is a natural plant polysaccharide obtained from plantago ovata and its mucilage is composed of neutral arabinoxylan (arabinose 22.6%, xylose 74.6%) [1]. Psyllium mucilage an anionic natural polysaccharide consisting of pentosan and uronic acid obtained from the seeds plantago psyllium [2-6]. Sodium salt of partially carboxymethylated is one of psyllium derivative and it is improve characteristics of psyllium such as increases swellability as well as reactivity to monomer and initiator [7-9]. Sodium salt of partially carboxymethylated (Na-PCMPsy) shows numerous applications in the field of biodegradable, textile, medicinal and hydrogels. Grafting techniques have received considerable attention from scientists all over the world, especially regarding those systems in which a natural polymer is a polysaccharide probably due to its abundant availability and low cost. The photo-induced graft copolymerization technique is most promising and practical method because of its simplicity. The graft copolymerization by low energy UV- radiation possesses certain advantages like less degradation of the backbone polymer and control over the reaction. Photo-induced graft copolymerization of vinyl monomers onto polymer backbones has many advantages as compared to other methods of grafting by free

radical polymerization. This technique showed a controlled generation of radical sites on polymer backbones in addition to attaining higher grafting efficiencies [10-12]. In present work we have synthesize, characterize and optimize the reaction parameters for photo-graft polymerization between acrylonitrile and sodium salt of partially carboxymethylated psyllium. Photo graft copolymers were essentially characterized by infrared spectroscopy, scanning electron microscopic and thermo gravimetric analysis.

MATERIALS AND METHOS

Psyllium was supplied by Gujarat Sat-Isabgol Factory, Unjha (Gujarat/India). Sodium salt of Partially Carboxymethylated Psyllium was prepared from Psyllium and purification as well as the measurement of degree of substitution was followed as discussed earlier [13]. The \overline{DS} was found to be 0.13. Acrylonitrile (AN) (Fluka) was distilled out at atmospheric pressure and the middle fraction was collected. Ceric ammonium nitrate, CAN (Analar grade, Qualigens, Glaxo India Ltd) was used as photo-initiator. All other reagents and solvents used were of reagent grade. Nitrogen gas was purified by passing through freshly prepared alkaline pyrogallol solution. The conductivity water was used for the preparation of solutions as well as in polymerization reactions.

Instrument

The UV-radiation source was purchased from Scientific Aids and Instruments Corporation (SAIC), Madras. The UV-reactor was then assembled with immersion well containing 125 W medium pressure mercury lamps. The medium pressure lamps have much more intense arcs and radiate predominantly 254, 365, or 425 nm radiation.

Synthesis

The photo-induced graft copolymerization reactions were carried out in 500 mL glass vessel. A weighed amount of Na-PCMPsy (0.2-1.0g) was dissolved in 144.28 mL of conductivity water in the photochemical reactor and the solution was stirred with continuous bubbling of a slow stream of nitrogen gas for an hour at 55°C and thereafter 20 minutes at room temperature. 2.5 mL of freshly prepared CAN solution ($0.5 \times 10^{-3} - 10.0 \times 10^{-3}$ mol/L) in nitric acid (Nil-0.5 mol/L) was added to the photochemical reactor and contents were also then flushed with purified nitrogen gas and freshly distilled AN (0.037 – 0.370 mol/L) was added and put the reaction vessel in the UV- reactor cabinet. The solution thus was irradiated with continuous stirring for different time intervals (0.5 – 10 h) in the temperature range 20-45°C. After completion of the grafting reaction the irradiated sample solution was removed carefully and the crude graft product was isolated by centrifugation. It was then purified by washing with dilute nitric acid as well as 90% methanol and finally washed with pure methanol. The crude copolymer sample of Na-PCMPsy-g-PAN thus obtained was dried under vacuum at 40°C. The homopolymer was removed from the crude graft copolymer by exhaustive soxhlet extraction with dimethyl formamide for 48 h.

IR Spectra

IR spectra of Psyllium, Na-PCMPsy ($\overline{DS} = 0.13$), Na-PCMPsy-g-PAN and PAN were taken in KBr pellet using Nicolet Impact 400 D Fourier Transform Infra Red Spectrophotometer.

Thermogravimetric Analysis (TGA)

The thermal behavior of Psyllium, Na-PCMPsy ($\overline{DS} = 0.13$), Na-PCMPsy-g-PAN and PAN has been examined in an inert atmosphere at a heating rate of 10⁰C/min. with the help of the Mettler Toledo Star SW 7.01 thermogravimetric analyzer.

Scanning Electron Microscopy (SEM)

Model ESEM TMP + EDAX, Philips make has been used to obtain the micrographs of Psyllium, Na-PCMPsy ($\overline{DS} = 0.13$) and Na-PCMPsy-g-PAN graft copolymer samples.

RESULTS AND DISCUSSION**Optimum Reaction Conditions***Effect of backbone concentration*

Photo grafting of acrylonitrile (AN) onto Na-PCMPsy (Fig.1) the value of grafting (%G) as well as grafting efficiency (%GE) are found to be increased with increase in Na-PCMPsy concentration and the maximum value is reached at 0.6 gm of Na-PCMPsy concentration. Beyond this optimum concentration of Na-PCMPsy, %G and %GE values are found to be decreased with further increase in Na-PCMPsy concentration. The greater the amount of Na-PCMPsy for a given amount of monomer, the greater is the amount of complex formed during the course of irradiation, and consequently, the higher is the number of active sites generated on the polymeric substrate during the subsequent decomposition of the complex. As a result of this the grafting yields are found to be increased with the increase in the backbone concentration. The observed decrease in %G as well as %GE with the further increase in the amount of Na-PCMPsy indicates the formation of homopolymer.

Effect of photo-initiator concentration

The effect of the photo-initiator concentration of Ce^{+4} ions on the grafting yields is shown in Fig. 2. It can be seen from this figure that with increasing ceric-ion concentration, %G and %GE are found to increase and reaches maximum value of 151.51% at $[Ce^{+4}] = 6.0 \times 10^{-3}$ mol/L, however, with further increase in $[Ce^{+4}]$, the values of %G and %GE are decreases. Thus, the observed increase in %G within the photoinitiator concentration (CAN) range $0.5 \times 10^{-3} - 6.0 \times 10^{-3}$ mol/L may be due to the fact that within these concentration range, the complex formation between the -OH groups as well as carboxylate anion of Na-PCMPsy and Ce^{+4} is facilitated and the photo decomposition of the complex leads to the formation of more active sites. Thus, this activation along the backbone which has taken place is immediately followed by the graft copolymerization of AN onto the Na-PCMPsy. The observed decrease in the grafting yields (%G as well as %GE) at higher photoinitiator concentration, i.e. beyond $[Ce^{+4}] = 6.0 \times 10^{-3}$ mol/L, may be due to the efficiency of Ce^{+4} to take part in the termination of growing grafted chains. Furthermore, homopolymer (PAN) formation at higher initiator concentration which competes with the grafting reaction for the available monomer (AN) could also lead to a decrease in %G as well as %GE. Similar results are also reported in the literature [14-16].

Effect of acid concentration

The photo-grafting of AN onto Na-PCMPsy at different nitric acid concentrations is shown in fig. 3. It can be observed from the figure that there is an optimum concentration of nitric acid at 0.1 mol/L which affords maximum percentage of grafting. The values of %G and %GE are found to be decreased beyond the optimum concentration of nitric acid. It is interesting to note that even at zero concentration of nitric acid, an appreciable value of percentage of grafting is observed this may be due to the possibility that, even in absence of acid, in an aqueous medium Na-PCMPsy ionizes fully to a greater extent which facilitates the diffusion of monomer as well as photoinitiator leading to appreciable values of grafting. The values of %G and %GE increase in the beginning with increase in nitric acid concentration may be due to decrease termination rate of the growing polymer chain, or an increase in the initiation rate. However, beyond the optimum concentration of acid, the decrease in %G and %GE could be attributed to a

corresponding reduction in ceric-Na-PCMPsy complex formation, as well as an increase in termination rates [17, 18].

Effect of monomer concentration

It can be observed from (Fig. 4) that with an increase in the concentration of monomer, percentage of grafting increases and reaches a maximum value of 353.16 at a monomer concentration 0.332 mol/L. Beyond this optimum value, the grafting yields (%G and %GE) are found to be decreased with further increase in the monomer concentration. The increase in the value of %GE by increasing the monomer concentration could be attributed to the greater availability of grafting sites to monomer. However, the decreasing trend of %GE as shown in fig.4 is probably due to the competition between the homopolymerization and grafting where the former prevails over the latter at higher monomer concentration.

Effect of Temperature

It can be observed from the (Fig. 5), the values of the grafting yields (%G and %GE) are found to be increased from 20⁰C to 30⁰C in case of acrylonitrile monomer. Thus, the observed increase in %G as well as %GE with temperature could be interpreted in terms of favorable influence of temperature on: (a) the faster photolysis of the Na-PCMPsy-Ceric complex so that more active sites are generated on the Na-PCMPsy chains; (b) the swellability of Na-PCMPsy ; (c) solubility of monomer molecules ; (d) diffusion rate of monomer from the aqueous phase to the backbone; and (e) the rates of initiation and propagation of photografting.

The observed decrease in grafting efficiency with rising temperature may also be attributed to the solubility of monomer in the aqueous phase at higher temperatures, thus increasing the possibility of the monomer to contact Ce(IV), hence more Ce(IV) will be available to initiate the homopolymerization. In addition, at higher temperatures, various hydrogen abstraction and chain transfer reactions might be accelerated which may lead to decrease in %G as well as %GE.

Effect of Reaction Time

The values of %G and %GE obtained in the case of photo-graft copolymerization of AN onto Na-PCMPsy at various reaction times are shown in fig. 6 represent the influence of reaction time on %G as well as % GE. It can be observed from the fig. 6 that the values of %G and %GE are found to be increased in the beginning and achieved the maximum value of the grafting 133.59% at 2 h. However, beyond these optimum value, %G and %GE are found to be decreased with further increase in time. The result of this figure may be explained on the basis of the fact that with increase in reaction time the number of grafting sites on the backbone increases as a result of which the extent of initiation and propagation of photo-graft copolymerization also increases with time leading to the increase in the grafting yields. But beyond the optimum value of reaction time (i.e. 2 h) as the available sites for photo-grafting of the corresponding monomer on the Na-PCMPsy backbone get reduced, the decrease in the value of % G as well as the decrease in % GE values is observed. The observed decrease in the values of grafting yields is also may be presumably due to the detrimental effect of UV-radiation onto the grafted side chains PAN at longer irradiation times in the presence of the photoinitiator. In addition to this the decrease in the values of %G and % GE beyond optimum reaction time may also be attributed to the depletion in monomer and initiator concentrations as well as shortage of the available grafting sites.

Evaluation of Energy of Activation

The natural log of % grafting (ln %G) versus 1/T is plotted for the initial portion of the curve, i.e. 20-30⁰C (cf. Figure 5) as shown in Figure 7 and these values are found to fall on a straight line as

is evident from this figure. The least square value of the overall activation energy of grafting (E_g) is calculated from the results of Fig. 7 and is found to be 8.31 KJ/mol [19].

Characterization

FT-IR Spectroscopy

FT-IR spectral analysis was used to confirm the graft copolymerization reaction. The FT-IR spectrum of pure psyllium (Fig. 8) shows the characteristic peak at 3407 cm^{-1} due to $-\text{OH}$ stretching, $-\text{C}=\text{O}$ of $-\text{COOH}$ at 1640 cm^{-1} and ether linkage at 1465 cm^{-1} . FT-IR spectrum of Na-PCMPsy (Fig.9) shows characteristic peaks at 1605 and 1423 cm^{-1} respectively due to asymmetric and symmetric vibration of $-\text{COOH}$ group. This can be attributed to the incorporation of carboxymethyl groups in psyllium. FT-IR spectrum of Na-PCMPsy-g-PAN (Fig. 10) shows characteristic peaks of $-\text{OH}$ at 3424 cm^{-1} , $-\text{C}=\text{O}$ of $-\text{COOH}$ at 1658 cm^{-1} and ether linkage at $1456\text{--}1384\text{ cm}^{-1}$, and most promising band at 2244 cm^{-1} due to the nitrile ($\text{C}\equiv\text{N}$) group.

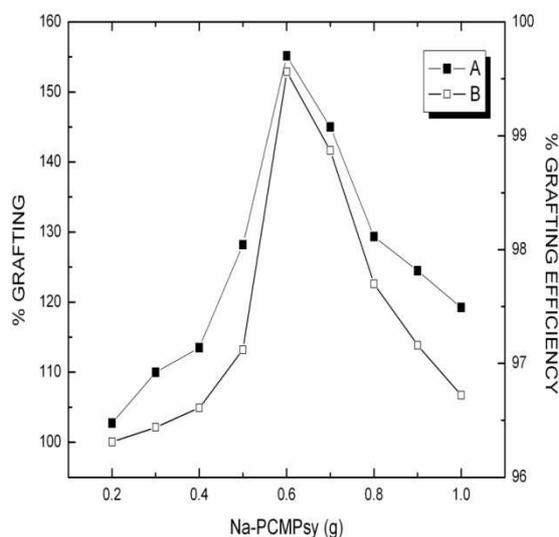


Fig.1 Effect of Na-PCMPsy on: (A)-%G; or (B)-%GE

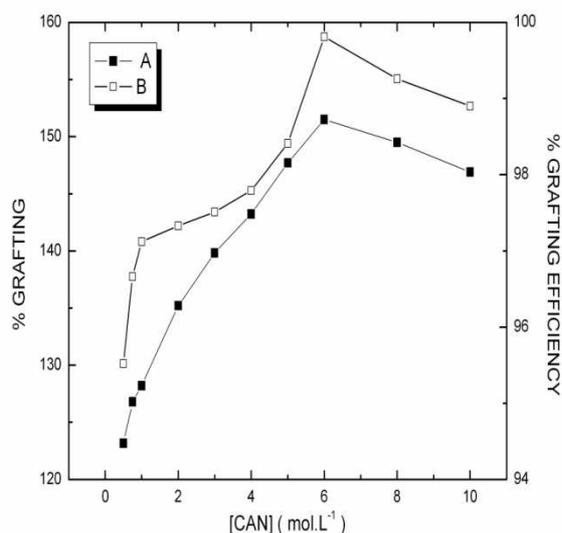


Fig.2 Effect of Cerium Ammonium Nitrate Concentration on: (A)-%G; or (B)-%GE

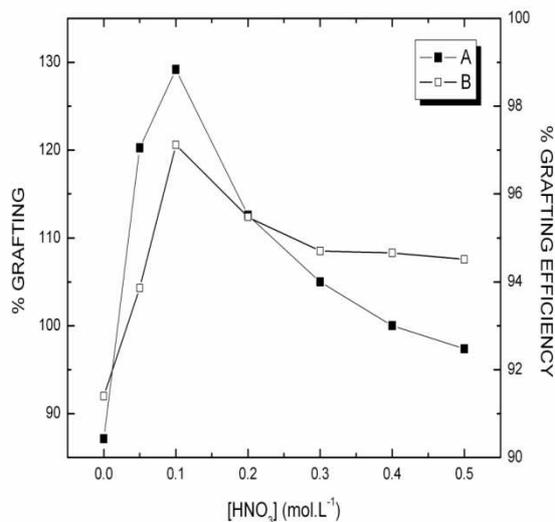


Fig.3 Effect of nitric acid concentration on: (A)-%G; or (B)-%GE

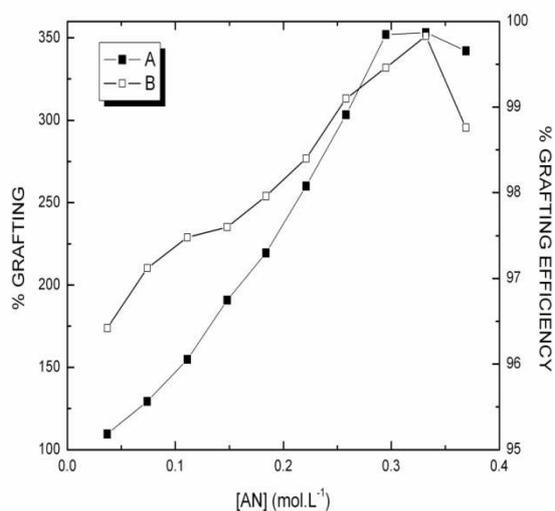


Fig.4 Effect of acrylonitrile concentration on: (A)-%G; or (B)-%GE

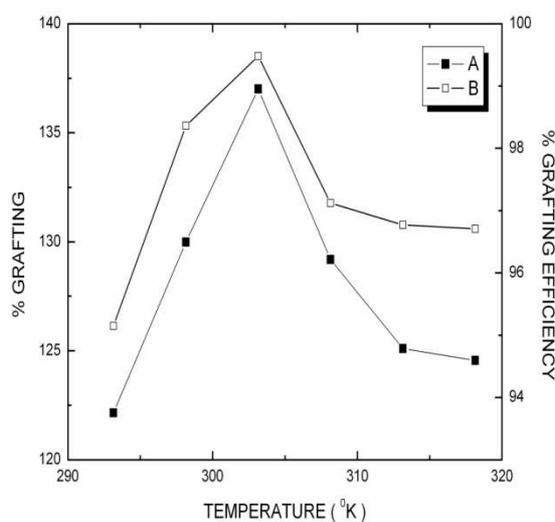


Fig.5 Effect of temperature on: (A)-%G; or (B)-%GE

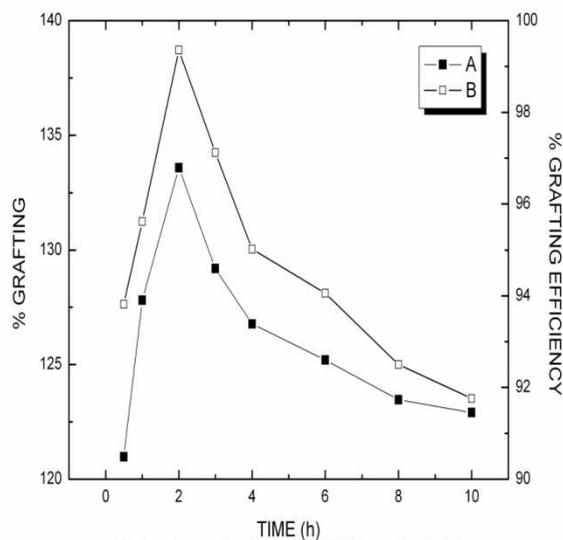


Fig.6 Effect of reaction time on: (A)-%G; or (B)-%GE

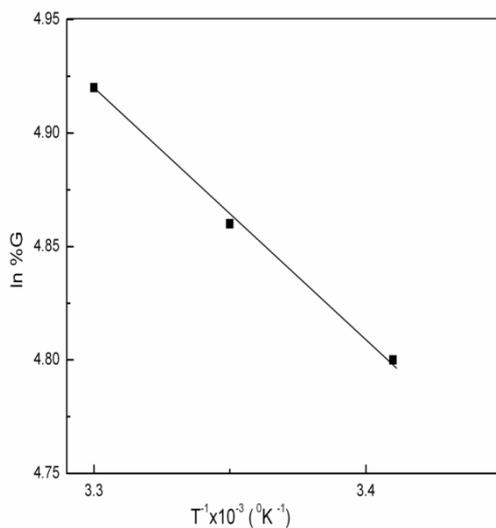


Fig.7 Plot of natural log of percentage grafting versus 1/T

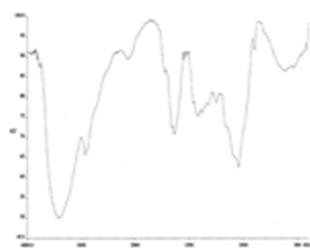


Fig. 8. IR spectrum of psyllium

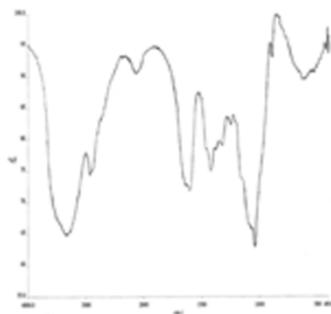


Fig. 9. IR spectrum of Na-PCMPsy

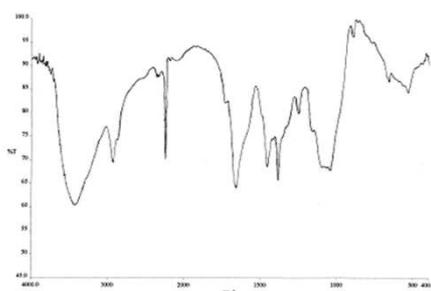


Fig. 10. IR spectrum of Na-PCMPsy-g-PAN

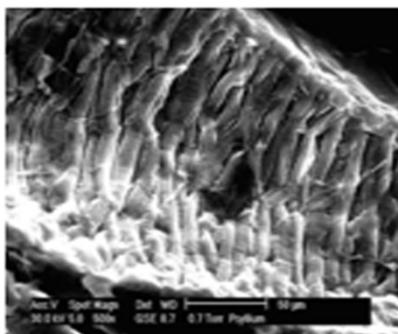


Fig. 11. Scanning Electron Micrograph of Psyllium (500X)

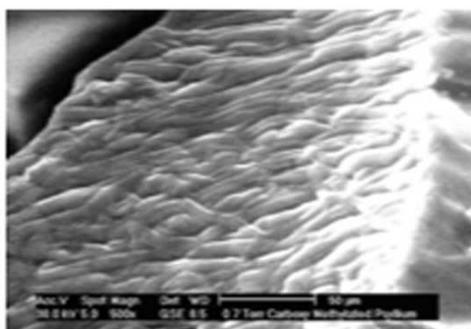


Fig. 12. Scanning Electron Micrograph of Na-PCMPsy ($\overline{DS} = 0.13$) (500X)

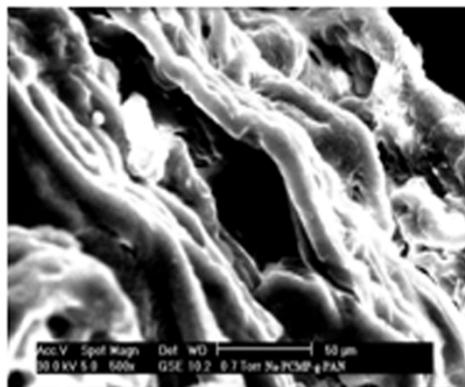


Fig. 13. Scanning Electron Micrograph of Na-PCMPsy-g-PAN (500X)

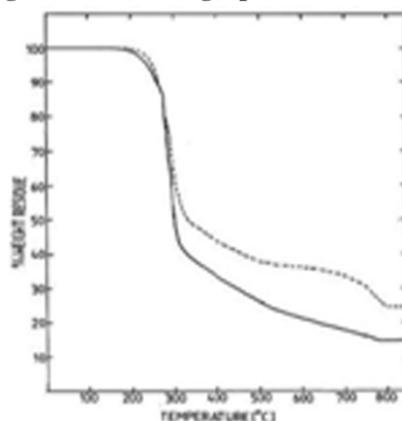


Fig. 14. Thermogram for Psyllium and Na-PCMPsy

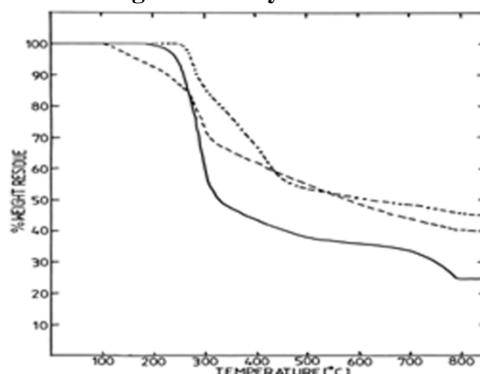


Fig. 15. Thermogram for (—) Na-PCMPsy, (-----) Na-PCMPsy-g-PAN (%G =424.51) and (—●—●—) PAN at 10°C/min

Table 1: Thermal analysis of Psyllium, Na-PCMPsy, Na-PCMPsy-g-PAN and PAN samples.

Sample	Thermogravimetric analysis data		Tmax (°C)		T ₁₀ (°C)	T ₅₀ (°C)	IPDT
	Ti °C (IDT)	Tf °C (FDT)	Step 1	Step 2			
Psyllium	170	780	295	-	265	300	475
Na-PCMPsy	190	790	300	-	260	330	538
Na-PCMPsy-g-PAN	110	790	255	465	230	590	599.6
PAN	250	790	365	-	280	620	633.4

Scanning Electron Microscopy (SEM)

The scanning electron micrograph of psyllium (Fig. 11) shows fiber-like appearance structure. Upon carboxymethylation of psyllium, the structure of psyllium gets improved as shown in (Fig. 12), wherein the morphology of the fiber-like structure is modified in such a way that because of

the introduction of the hydrophilic groups onto psyllium, the fibers seem to have got swollen and exhibited smooth surface, and after grafting it is clearly evident that the grafted chains have drastically changed the topology of the Na-PCMPsy. As shown in (Fig. 13) stiff morphology with lower adhering characteristics is observed with grafting of acrylonitrile (AN) onto Na-PCMPsy.

Thermogravimetric analysis (TGA)

Fig. 14 show the primary thermograms of Psyllium and Na-PCMPsy obtained at a scan rate $10^{\circ}\text{C}/\text{min}$. The overall degradation of Psyllium (Fig.14) involves only single step. The sample begins to decompose at 170°C , rapidly loses 57.5 % of its weight upto 315°C . Beyond 315°C , the weight loss is slow and gradual upto about 780°C leaving 14.5 % residual weight. In the temperature range $315\text{-}780^{\circ}\text{C}$, the sample loses 28 % of its original weight. The maximum rate of weight loss occurs at 295°C . In the case of Na-PCMPsy (Fig. 14) also a single step of degradation is observed. The decomposition starts at 190°C and proceeds at a faster rate upto 320°C and at this temperature the sample loses 48% of its original weight. However, beyond this temperature, degradation proceeds at a slow rate upto 500°C compared to the degradation proceeded in the earlier temperature range. This temperature range involves about 14% weight loss. With further increase in temperature, the degradation is found to occur at a relatively very slow rate upto 790°C . The temperature at which the maximum rate of weight loss occurs is at 300°C . The overall degradation leaves about 24.5% residue.

Fig. 15 shows the primary thermograms obtained at a scan rate of $10^{\circ}\text{C}/\text{min}$ for Na-PCMPsy, Na-PCMPsy-g-PAN (%G =424.51) and PAN, in an inert atmosphere. Na-PCMPsy-g-PAN involves two steps of degradation. The first step of degradation begins at 110°C and proceeds slowly upto 300°C involving about 27% weight loss with a maximum rate of weight loss at 255°C . The second decomposition step comprises of $300\text{-}790^{\circ}\text{C}$ involving about 32% weight loss with a maximum rate of weight loss at 465°C . The sample leaves about 40% residue weight. In the case of PAN (Fig. 15) the overall degradation involves only single step. The degradation occurs in the temperature range $250\text{-}790^{\circ}\text{C}$ involving about 54% weight loss with a maximum rate of weight loss at 365°C . The final residue at 790°C amounts to about 45.5%.

The temperature characteristic values as well as the value of the integral procedural decomposition temperature (IPDT) of psyllium, Na-PCMPsy ($\overline{\text{DS}} = 0.13$), Na-PCMPsy-PAN and PAN are tabulated in Table 1. The examination of IPDT values indicates that the overall thermal stability of psyllium has been increased upon its carboxymethylation this may be due to introduction of polar groups into it leading to the increased inter-molecular and intra-molecular interactions which ultimately imparts higher thermal stability to it as well as in case of graft copolymers and homopolymer (Na-PCMPsy-PAN and PAN), the observed IPDT value is increases as compared to psyllium and Na-PCMPsy, this may be due to increased in ring formation at higher temperatures may be responsible for this greater stability.

CONCLUSION

Photo-induced grafting of PAN has been successfully carried out onto Na-PCMPsy ($\overline{\text{DS}} = 0.13$) using CAN as a photo-initiator and the optimized reaction conditions have been evaluated. Under the optimized reaction conditions the maximum values of the grafting yields are %G= 424.51 and %GE= 99.72. The spectral (IR), TGA as well as SEM techniques have been employed successfully as the evidence of photo-induced grafting.

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