

Photo-Induced Sodium salt of Partially Carboxymethylated Psyllium-g-Polyacrylonitrile: I. Synthesis and Characterization

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Abstract- An unreported photo-initiated graft copolymerization of acrylonitrile (AN) onto sodium salt of partially carboxymethylated psyllium (Na-PCMPSy, $\overline{DS} = 0.13$) was studied using uranyl nitrate (UN) as a photo-initiator. The Optimal reaction conditions for affording maximum percentage of grafting were evaluated by successively varying various reaction parameters viz. concentrations of photo-initiator, nitric acid and monomer as well as reaction time, temperature and amount of substrate. At the optimum reaction conditions the maximum values of the grafting yields achieved were %G = 219.62 and %GE = 99.85. The influence of various reaction parameters on the grafting yields was studied. The reaction mechanism for photo-initiated synthesis of Na-PCMPSy-g-PAN was proposed. The photo-induced grafting copolymerization process was confirmed and the products were characterized by using FTIR, XRD and SEM techniques.

Index Terms- Acrylonitrile, Characterization, Photo-induced Grafting, Sodium salt of Partially Carboxymethylated Psyllium, Uranyl Nitrate

I. INTRODUCTION

The chemical modification of polymeric materials based on natural polysaccharides by grafting has received considerable attention in recent years because of the abundant availability, low cost and ecofriendly nature of the polysaccharides. Among grafting methods used, photo-grafting polymerization is widely known to be useful because of its significant advantages: less degradation of the backbone polymer, control over the grafting reaction in addition to attaining higher grafting efficiency, low cost of operation and selectivity to absorb UV light. Psyllium husk (PSy), whose scientific name is *Plantago ovata*, is a well known natural plant polysaccharide which is used in constipation, diarrhoea, cholesterol control, diabetes and colon cancer (Gupta, 1982). It is found to be a neutral arabinoxylan (arabinose 22.6%, xylose 74.6%, molar basis; only traces of other sugars), the highly branched polysaccharide, consisting of a densely substituted main chain of β -(1 \rightarrow 4)-linked D-xylopyranosyl units to which single units of α -L-arabinofuranose [via α -(1 \rightarrow 3) and/or α -(1 \rightarrow 2) linkages] and additional xylose are attached. Rhamnose, galactose, glucose and rhamnosyluronic acid residues are present as minor constituents (Fischer et al., 2004). Literature survey reveals that PSy has been suitably modified with other materials following grafting methods and used as flocculants (Mishra et al. 2002; Srinivasan et al.; 2002; Mishra et al., 2003; Mishra et al., 2004; Mishra et al., 2002; Mishra et al., 2004; Sen et al., 2012). However, due to the low solubility of PSy in cold water, poor solution clarity as well as the desire for products with modified or special properties, we have carried out carboxymethylation of PSy to obtain sodium salt of partially carboxymethylated psyllium (Na-PCMPSy) and reported first time in the literature the photo-grafting of methyl acrylate (MA) (Trivedi et al., 2009), acrylonitrile (AN) (Dholakia et al., 2011) and butyl acrylate (BA) (Dholakia et al., 2011) as well as methyl methacrylate (MMA) (Dholakia et al., 2012) onto it using ceric ammonium nitrate (CAN) as a photo initiator in an aqueous medium.

In the present study, the results on the evaluation of the optimal reaction conditions in the case of the photo-initiated graft copolymerization of AN onto Na-PCMPSy ($\overline{DS} = 0.13$) using uranyl nitrate as a photo-initiator in an aqueous medium have been reported. The effects of the reaction conditions on the grafting yields were also studied. FTIR, XRD and SEM techniques were used to characterize the products. However, the studies on the potential application of the synthesized graft copolymer (Na-PCMPSy-g-PAN) as superabsorbent has been carried out successfully and the interesting results regarding the swelling behaviour of the superabsorbent in different swelling media have been obtained and will be published in the following communication.

II. EXPERIMENTAL

2.1. Materials

Psyllium (PSy) was obtained from Sat-Isabgol factory (Unjha, Gujarat India). The methods of preparation and purification, as well as the measurement of degree of substitution (\overline{DS}) of sodium salt of partially carboxymethylated psyllium (Na-PCMPSy) were followed as described earlier (Dholakia et al., 2012). The \overline{DS} of Na-PCMPSy was found to be 0.13. AN (Fluka) was distilled out at atmospheric pressure and the middle fraction was collected and used. Uranyl nitrate (UN, Chiti Chem; Baroda, Gujarat, India) was used as received. Analar grade nitric acid was used. Fresh solutions of the photo-initiator were prepared by dissolving the required amount of UN in nitric acid. All other reagents and solvents used in the present work were of reagent grade. Nitrogen gas was purified by passing through fresh pyrogallol solution. Low conductivity water was used for the preparation of solutions as well as photo-graft copolymerization reactions.

2.2. Photo-graft copolymerization

The photo-graft copolymerization reactions were carried out in a photochemical reactor (Fig. 1) supplied by Scientific Aids and Instrument Corp. (SAIC, Madras, India) as per the procedure described earlier (Thaker and Trivedi, 2005). A weighed amount of Na-PCMPSy ($\overline{DS} = 0.13$, 0.2-1.0 g, dry basis) was dissolved in 144.28 mL of low conductivity water in the reaction flask and the solution was stirred with continuous bubbling of a slow stream of nitrogen gas for one hour at 55⁰C and thereafter for twenty minutes at room temperature. 2.5 mL of freshly prepared UN solution ($2 \times 10^{-3} - 10 \times 10^{-3}$ mol/L) in nitric acid (nil - 0.5 mol/L) was added to the reaction flask, and the contents were then flushed with purified nitrogen gas which was followed by the addition of freshly distilled AN (0.05-0.308 mol/L). The reaction flask was then assembled with an immersion well containing a 125W medium pressure mercury lamp. The whole assembly (photochemical reactor) was placed in a dark cabinet after covering it completely with aluminum foil. The lamp was then illuminated. Water from a constant-temperature water circulation bath was circulated over the immersion well and the reaction flask. The solution then was irradiated with continuous stirring for different time intervals (0.5-6h) in the temperature range of 20⁰C -50⁰C. After the completion of the grafting reaction, the irradiated sample solution was removed carefully, and the crude graft copolymer was isolated by centrifugation. It was then purified by washing with dilute nitric acid and repeated washings with 95% methanol and finally with pure methanol. The crude copolymer sample of Na-PCMPSy-g-PAN thus obtained was dried in vacuum at 40⁰C. The homopolymer, polyacrylonitrile (PAN), was separated from the crude graft copolymer by carrying out soxhlet extraction with dimethyl formamide for 48h. After the complete removal of the homopolymer, the pure graft copolymer was dried at 40⁰C in vacuum until a constant weight was obtained.

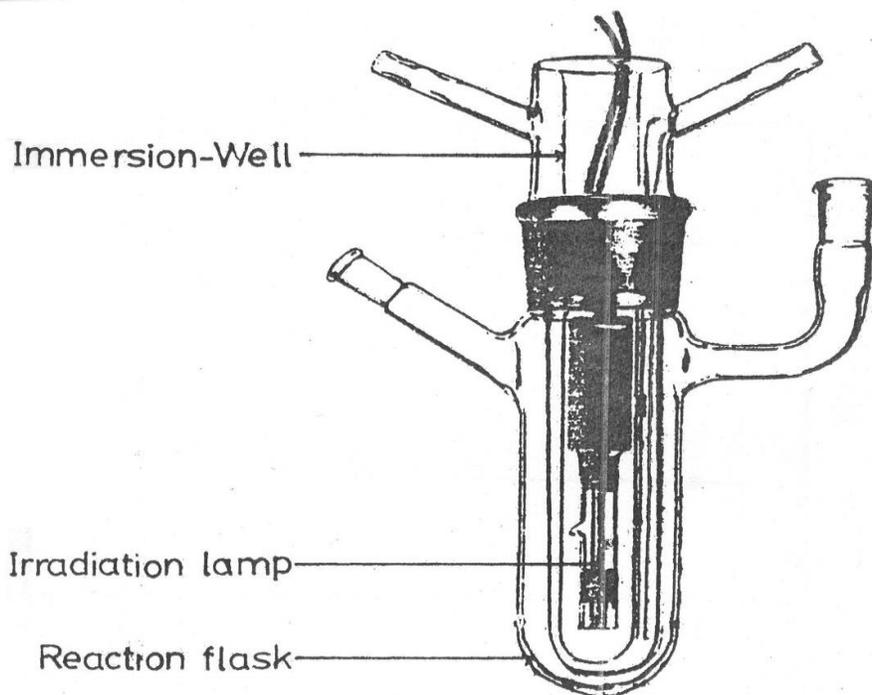
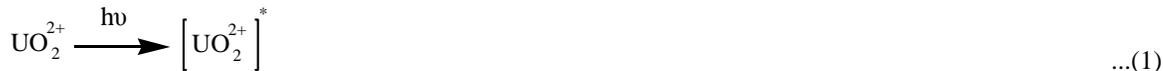


Figure 1: Photo Chemical Reactor

The free radical reaction mechanism of the photo-initiated graft copolymerization of acrylonitrile onto Na-PCMPSy ($\overline{DS} = 0.13$) using uranyl nitrate as a photo initiator is expected to proceed according to the Scheme 1.

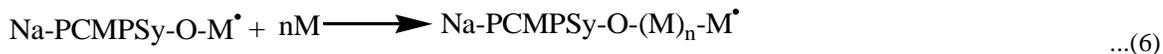
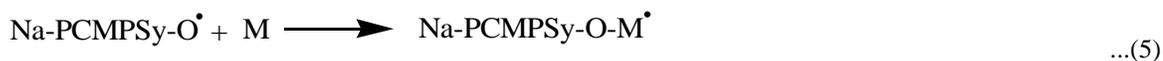
Radical Generation:



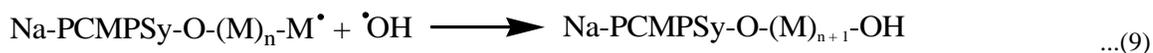
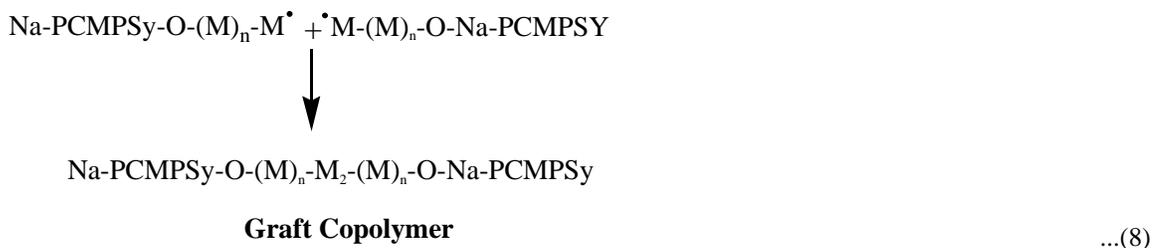
Initiation:



Propagation:



Termination:



Homopolymer

where Na-PCMPSy-O \cdot - Backbone free radical, M \cdot - monomer free radical

Scheme 1: Schematic representation of mechanism for photo-initiated synthesis of Na-PCMPSy-g-PAN

2.3. Grafting Parameters

Grafting parameters viz. percentage of grafting (%G) and percentage of grafting efficiency (%GE) were calculated by using the following expressions (Vora et al., 1995).

$$\% G = \frac{\text{Weight of grafted polymer}}{\text{Initial wight of backbone}} \times 10^2 \quad \dots(11)$$

$$\% GE = \frac{\text{Weight of grafted polymer}}{\text{Weight of grafted polymer} + \text{Weight of homopolymer}} \times 10^2 \quad \dots(12)$$

2.4. Isolation of grafted chains

The graft copolymer of Na-PCMPsy ($\overline{DS} = 0.13$) containing PAN was hydrolyzed by refluxing it for 12h in 1NHCl as described elsewhere (Brockway and Seaberg, 1967) for the isolation of the grafted PAN chains.

2.5. Characterization

2.5.1. Infrared (IR) spectroscopy

IR spectra of PSy, Na-PCMPsy ($\overline{DS} = 0.13$), Na-PCMPsy-g-PAN (%G = 219.62) and PAN were taken in KBr pellets using Excalibur 3100 (varian) spectrophotometer.

2.5.2. X-ray diffraction analysis

X-ray diffraction analysis of PSy, Na-PCMPsy ($\overline{DS} = 0.13$), Na-PCMPsy-g-PAN (%G = 219.62) and PAN was carried out by means of D & Focus (Bruker) powder diffractometer with a Cu K_{α} radiation source.

2.5.3. Scanning electron microscopy (SEM)

Model S-4300 (Hitachi) was used to obtain the micrographs of PSy, Na-PCMPsy ($\overline{DS} = 0.13$) and Na-PCMPsy-g-PAN (%G = 219.62) samples.

III. RESULTS AND DISCUSSION

3.1. Determination of optimum reaction conditions

In the present study of photo-induced graft copolymerization, various reaction conditions were varied to discover those optimum for grafting. The variables studied included amount of the backbone (Na-PCMPsy, $\overline{DS} = 0.13$), concentrations of photo-initiator (UN), nitric acid and monomer (AN) as well as reaction time and temperature.

3.1.1. Effect of backbone concentration

The influence of varying amount of Na-PCMPsy on the grafting yields (%G and %GE) is shown in Fig. 1(a). It can be observed from this figure that the value of %G increases initially with increase in the amount of Na-PCMPsy and reaches a maximum value of 174.50 at 0.5 g of Na-PCMPsy concentration. With a further increase in Na-PCMPsy concentration, %G decreases. However, the value of %GE remains almost constant in the whole range of Na-PCMPsy concentration studied. The initial increase in %G may be due to the fact that the reactive sites increase with increase in amount of Na-PCMPsy. The decrease is attributed to the destruction of radical activity on the backbone soon after it is formed because of termination between backbone-backbone and backbone-primary radicals. Thus, beyond optimum concentration of Na-PCMPsy (0.5 g), the termination rate of photo-graft-copolymerization becomes faster than the rate of initiation leading to the decrease in %G. Similar results are reported in the literature (Dholakia et al., 2011; Shah et al., 1995).

3.1.2. Effect of photo-initiator concentration

Fig. 1(b) shows the effect of the photo-initiator (UN) concentration on the grafting yields. As apparent from the figure, with all other reaction conditions kept constant, the value of %G increases to a maximum value (%G = 203) at [UN] = 4.15×10^{-3} mol/L. However, with further increase in the [UN], the %G decreases. The value of %GE is found to be almost constant in the whole range of photo-initiator concentration range studied. The behaviour with regard to the variation in %G may be explained on the basis of the fact that with increasing the photo-initiator concentration, more Na-PCMPsy macroradicals are generated and consequently more active sites on the Na-PCMPsy backbone could react with AN leading to increasing %G. On the other hand, beyond the optimum concentration of the photo-initiator, there is an abundance of free radicals, which would, terminate the propagation of the graft polymerization leading to a decrease in %G. Moreover, homopolymer formation at higher concentration of the photo-initiator competes with the grafting reaction for the available monomer and could also lead to a decrease in %G. Similar results are also reported in the literature (Trivedi et al., 2009; Dholakia et al., 2012; Thaker M D and Trivedi, 2005; Shukla et al., 1991; Shukla et al., 1992; El-Shrebiny, 2009; El-Shrebiny and Smith, 2010; El-Shrebiny and Smith, 2010).

3.1.3. Effect of acid concentration

The results of the grafting yields (%G and %GE) in the case of photo-grafting of AN onto Na-PCMPsy ($\overline{DS} = 0.13$) at different nitric acid concentrations are depicted in Fig.1(c). It is evident from this figure that there exists an optimum concentration of nitric acid (0.1 mol/L) which affords maximum %G as well as %GE. Beyond the optimum concentration of nitric acid, both the values, %G and %GE are found to be decreased. Interestingly even at zero concentration of nitric acid the value of %G is found to be 134% [cf. Fig. 1(c)] which may be due to the possibility that, even in the absence of acid, in an aqueous medium Na-PCMPsy ionizes fully to a greater extent which facilitates the diffusion of monomer as well as photo-initiator leading to higher value of grafting. Below the optimum concentration the observed increase in the values of %G and %GE with increase in nitric acid concentration may be

attributed to an increase in the initiation rate of photo-grafting. On the other hand, the tendency of grafting yields to decrease with increase in nitric acid concentration, beyond the optimum value (0.1 mol/L), could be associated with a fast rate of termination because of the increased rate of generation of free radical species as well as abundance of hydrogen protons. In addition, coagulation of colloidal homopolymer in solution at lower pH values would also retard diffusion of both monomer and photo-initiator thereby leading to the decreased grafting yields. Similar observations are reported in literature (Trivedi et al., 2009; Dholokia et al., 2012; Thaker and Trivedi, 2005; Trivedi et al., 2015).

3.1.4. Effect of monomer concentration

Fig. 1(d) shows the influence of acrylonitrile concentration on the grafting yields. It can be seen from this figure that in the beginning %G as well as %GE increase rapidly with increasing monomer concentration but beyond AN = 0.1 mol/L, %G increases gradually while %GE remains almost constant. The increase in %G with increasing monomer concentration is probably due to the gel effect i.e. the solubility of polyacrylonitrile in its own monomer and this could be more pronounced at higher monomer concentration. This causes hindrance in termination, particularly by coupling of growing polymer chains. Besides this, the gel effect also causes swelling of Na-PCMPSy, thus facilitating diffusion of monomer to growing grafted chains and the active sites of Na-PCMPSy backbone, thereby enhancing grafting.

However, as it can be seen from Fig. 1(d) that %GE remains almost constant with increasing monomer concentration beyond 0.1 mol/L indicating that even when %G is increased, it has not contributed to a progressive increase in grafting efficiency. This may be due to the fact that the grafted chains acting as diffusion barriers which may impede diffusion of monomer into the backbone leading to the non-availability of the appreciable amount of monomer for photo-grafting. As a result of this there will be correspondingly homopolymer formation besides photo-grafting also, which has a leveling effect in %GE beyond 0.1 mol/L. Similar results are also reported in the literature (Trivedi et al., 2009; Trivedi et al., 2005; Shah et al., 1994).

3.1.5. Effect of reaction temperature

The photo-grafting reactions were carried out at different temperatures between 20°C and 45°C, keeping all other variables constant. Fig. 1(e) represents the influence of temperature on the grafting yields. It can be seen from this figure that in the temperature range 20°C -35°C, there is an increase in the grafting yields with increase in temperature but beyond 35°C they decrease with further increase in temperature. This observed increase in the grafting yields with temperature can be interpreted in terms of the favourable influence of temperature on: (i) the swellability of Na-PCMPSy (ii) the solubility of monomer molecules (iii) the diffusion and mobility of the monomer from the aqueous phase to the Na-PCMPSy backbone and (iv) the rates of initiation and propagation of photo-grafting.

The observed decrease in grafting yields beyond 35°C can be ascribed to the fact that at higher temperature graft copolymerization occurs with poor selectivity. In addition, various hydrogen abstraction and chain transfer reactions also might be accelerated at higher temperature leading to the decrease in the grafting yields. Similar results are also reported in the literature (Dholokia et al., 2011; Dholokia et al., 2011; Shukla et al., 1991; Shukla et al., 1992; Trivedi et al., 2012)

3.1.6. Effect of reaction time

Fig. 1(f) illustrates the effect of reaction time onto the grafting yields. It is interesting to note from this figure that a value of 157% has been obtained for %G in the first half an hour only. However, %G further increases up to a maximum of 197% within 2h. Beyond this optimum time, the value of %G decreases. On the other hand %GE increases up to 2h and then decreases with further increase in time up to 3h, beyond which it remains almost constant. Thus, the observed increase in the grafting yields up to 2h can be explained on the basis of the fact that with increase in reaction time, the number of grafting sites on the Na-PCMPSy backbone increases as a result of which the extent of initiation and propagation of photo-graft copolymerization also increases with reaction time leading to the increase in the grafting yields. On the other hand the observed decrease in %G and %GE, beyond the optimum reaction time, may be presumably due to the detrimental effect of UV radiation onto the grafted side chains of PAN at longer irradiation times in the presence of the photo-initiator. Besides, beyond the optimum reaction time, the depletion of monomer and photo-initiator concentrations as well as shortage of the available grafting sites may lower the grafting yields. Similar results are reported in the literature (Dholokia et al., 2012; Shukla et al., 1991; Shukla et al., 1992; Trivedi et al., 2015).

Thus, from the foregoing discussion, the optimum reaction conditions evaluated for affording maximum percentage of grafting in the case of photo-initiated graft copolymerization of AN onto Na-PCMPSy ($\overline{DS} = 0.13$) are : Na-PCMPSy ($\overline{DS} = 0.13$) = 0.5 g (dry basis), $[UN] = 4.15 \times 10^{-3}$ mol/L, $[HNO_3] = 0.10$ mol/L, $[AN] = 0.222$ mol/L, Temperature = 35°C, Reaction Time = 2h and Total Volume = 150 mL.

At the optimum reaction conditions, the maximum values of the grafting yields achieved were : %G = 219.62 and %GE = 99.85.

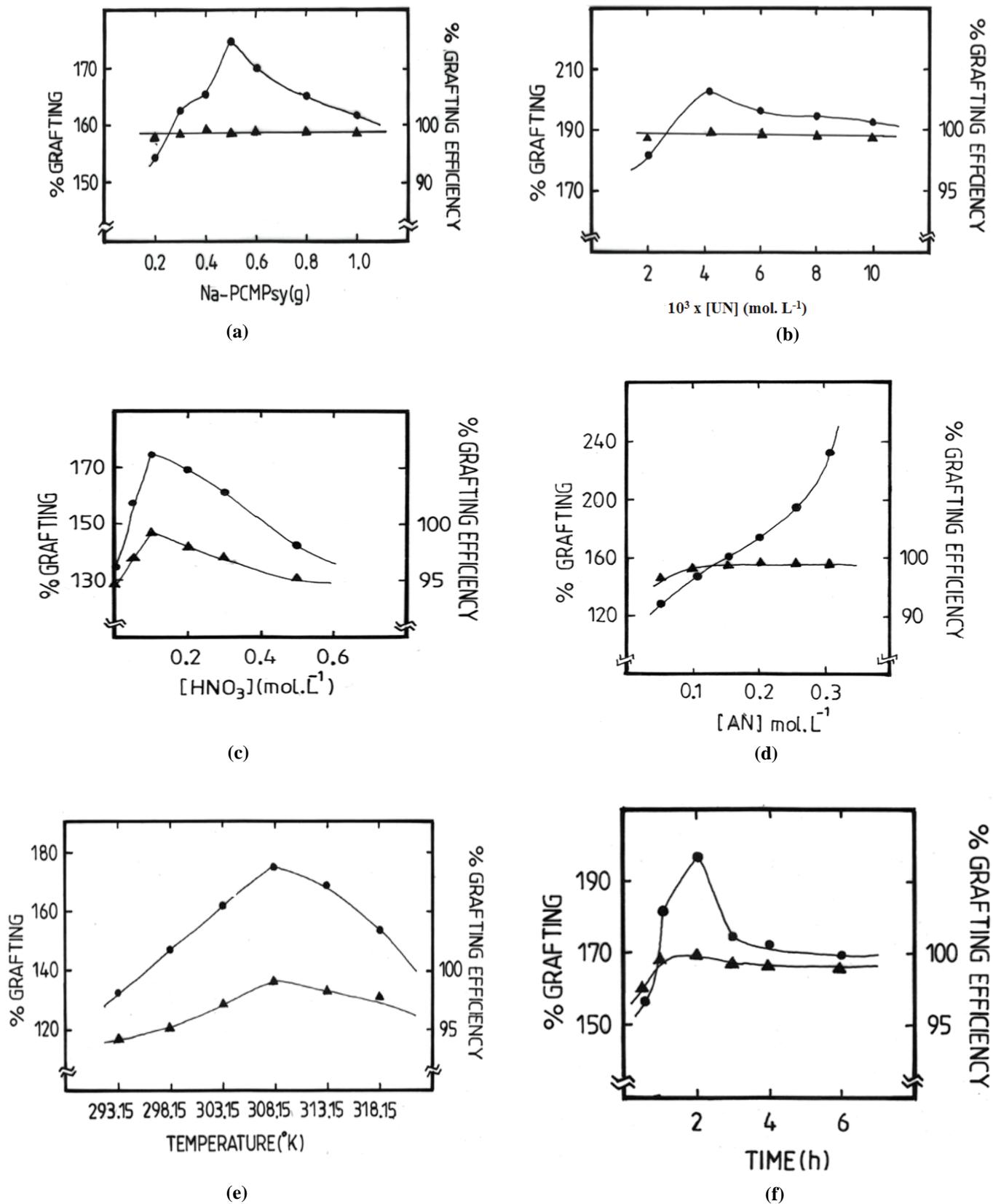


Figure 1. Influence of (a) amount of sodium salt of partially carboxymethylated psyllium; (b) uranyl nitrate (UN) concentration; (c) nitric acid concentration; (d) acrylonitrile (AN) concentration; (e) reaction temperature and (f) reaction time on: (●) - %G; or (▲) - %GE.

IV. CHARACTERIZATION

4.1. FTIR spectroscopy

The IR spectrum of PSy [Fig. 2(a)] shows very strong and broad peak at 3435.2 cm^{-1} which is assigned to the stretching vibration modes of $-\text{OH}$ groups. The small peaks at 2924 cm^{-1} and at 1731 cm^{-1} are assigned respectively to the $-\text{CH}$ stretching vibrations of CH_2 group and $\text{C}=\text{O}$ stretching vibrations. The absorption band appeared at 1633.5 cm^{-1} is due to hydration of water. The smaller peaks appeared at 1384.2 cm^{-1} and at 895 cm^{-1} are due to CH , CH_2 as well as OH in-plane bending in carbohydrates and pyranose rings respectively. The band at 1046.7 cm^{-1} is due to the $\text{C}-\text{O}$ stretching region as complex bands, resulting from $\text{C}-\text{O}$ and $\text{C}-\text{O}-\text{C}$ stretching vibrations.

Fig. 2(b) represents the IR spectrum of Na-PCMPSy with somewhat reduced intensity of the absorption band at 3421 cm^{-1} , due to OH stretching, indicating that some of the OH groups present in PSy are involved in carboxymethylation. The presence of band at 2925 cm^{-1} is due to $-\text{CH}$ stretching. The asymmetric and symmetric vibrations due to $-\text{COO}-$ moiety are assigned at 1609.03 cm^{-1} and 1420 cm^{-1} respectively. This can be attributed to the incorporation of carboxymethyl groups in PSy.

Figs. 2(c) and 2(d) show the IR spectra of Na-PCMPSy-g-PAN and PAN (isolated by hydrolysis method) samples respectively. The spectrum of the graft copolymer [Fig. 2(c)] showed absorption bands of Na-PCMPSy ($\overline{\text{DS}} = 0.13$) [Fig. 2(b)] as well as an additional band at $\sim 2244\text{ cm}^{-1}$, which has been attributed to $-\text{C}\equiv\text{N}$ stretching mode, characteristic of the spectra of PAN [Fig. 2(d)]. Thus, the presence of an additional band at $\sim 2244\text{ cm}^{-1}$ in the graft copolymer i.e. Na-PCMPSy-g-PAN indicates beyond doubt that photo-grafting of AN onto Na-PCMPSy ($\overline{\text{DS}} = 0.13$) has taken place. In the IR spectrum of the graft copolymer [Fig. 2(c)] the absorption band appeared at 1449.2 cm^{-1} is attributed to the presence of ether linkage. In comparison with the IR spectrum of Na-PCMPSy ($\overline{\text{DS}} = 0.13$) [Fig. 2(b)], somewhat broad absorption band appeared at 3423 cm^{-1} , due to $-\text{OH}$ stretching, in the case of the graft copolymer [cf. Fig. 2(c)] indicating the polymeric association also.

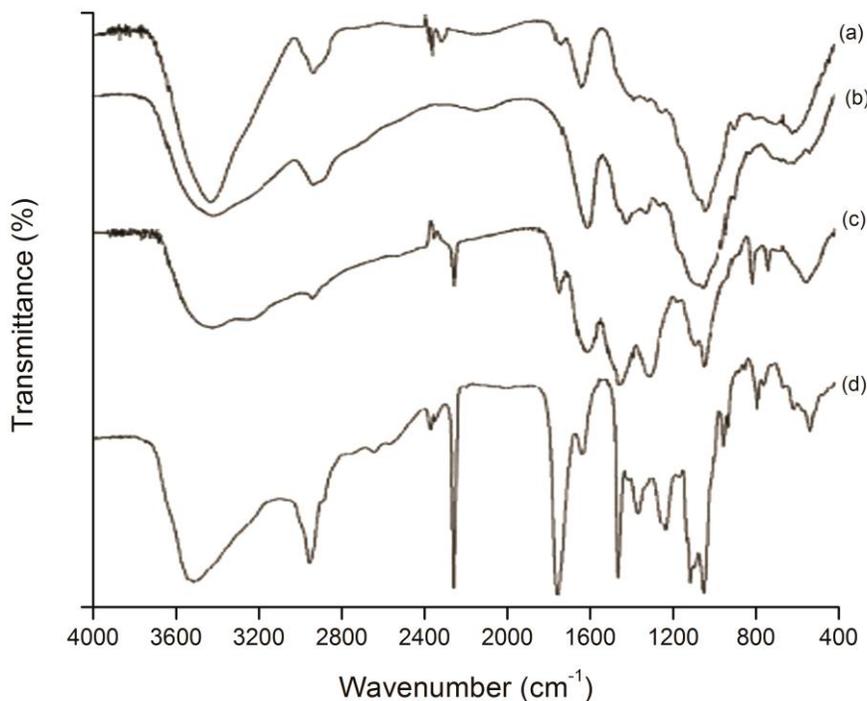


Figure 2: FTIR Spectra of (a) Psyllium (PSy), (b) Na-PCMPSy ($\overline{\text{DS}} = 0.13$), (c) Na-PCMPSy-g-PAN ($\%G = 219.62$) and (d) PAN

4.2. X-ray diffraction analysis

The powder X-ray diffractograms of PSy, Na-PCMPSy ($\overline{\text{DS}} = 0.13$), Na-PCMPSy-g-PAN and PAN are shown in Figs. 3(a) to (d). It can be evident from this figure that the patterns show the complete amorphous nature of PSy and Na-PCMPSy ($\overline{\text{DS}} = 0.13$). In the case of PAN, the crystalline peaks are observed in 2θ range $13-30^\circ$. The strongest diffraction peak appeared at $2\theta = 16.95^\circ$ and $2\theta = 29.39^\circ$ for PAN are due to the ordered crystal structures made up of PAN linear macromolecules. The XRD pattern of Na-PCMPSy-g-PAN is different from Na-PCMPSy ($\overline{\text{DS}} = 0.13$) and PAN. However, appearance of two weak peaks at $2\theta = 17.29^\circ$ and $2\theta = 28.63^\circ$,

which are very close to the diffraction peak characteristics of PAN (which happened to appear at $2\theta = 16.95^\circ$ and $2\theta = 29.39^\circ$), may be attributed to the occurrence of crystallization of PAN chains to some extent during graft copolymerization.

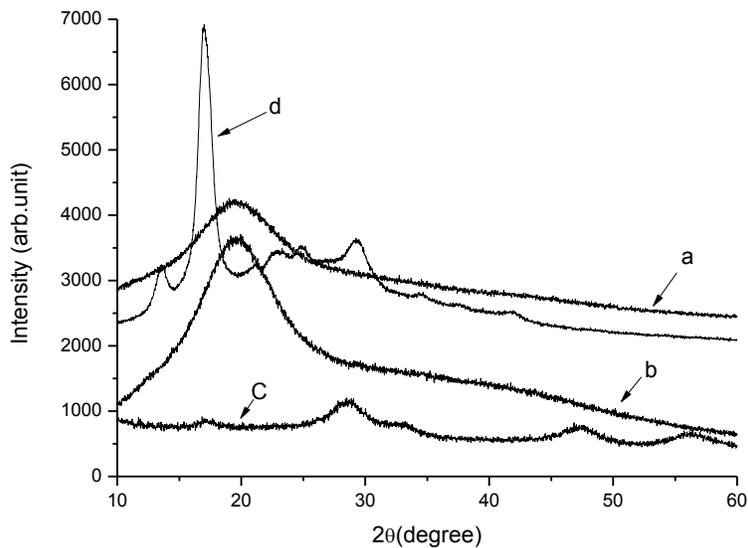


Figure 3: X-Ray diffraction patterns of (a) Psyllium (PSy), (b) Na-PCMPSy ($\overline{DS} = 0.13$), (c) Na-PCMPSy-g-PAN ($\%G = 219.62$) and (d) PAN samples.

4.3. Scanning Electron Microscopy (SEM)

The scanning electron micrograph of psyllium [Fig. 4(a)] shows fiber-like appearance structure. Upon carboxymethylation of psyllium, the structure of psyllium gets improved as shown in Fig. 4(b), wherein the morphology of the fiber-like structure is modified

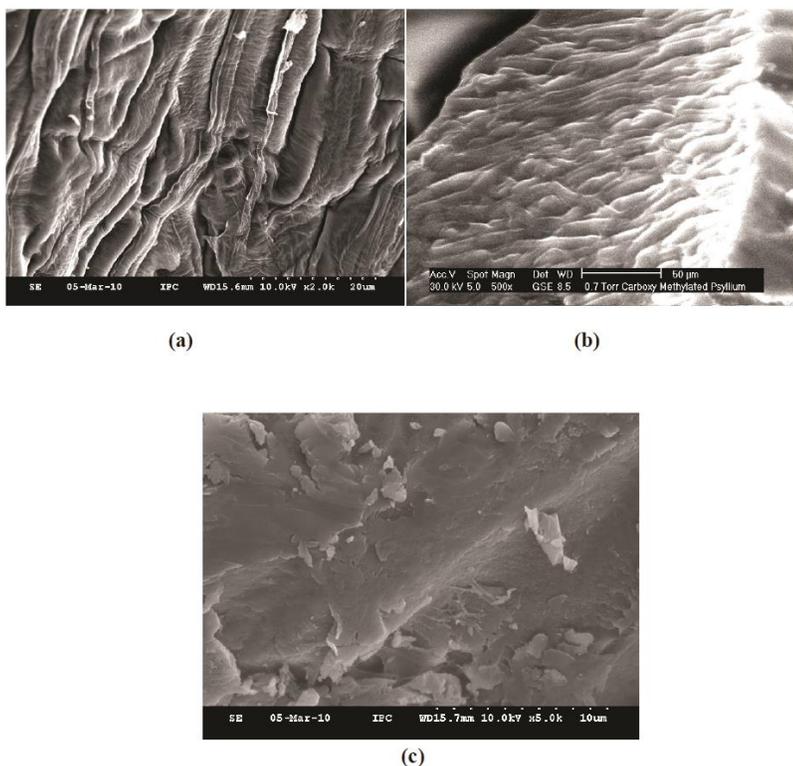


Figure 4: Scanning Electron Micrographs of (a) Psyllium (X 2.0k), (b) Na-PCMPSy ($\overline{DS} = 0.13$) (X500) and (c) Na-PCMPSy-g-PAN ($\%G = 219.62$) (X 5.0k) samples.

in a 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. The surface topology of Na-PCMPsy-g-PAN is shown in Fig. 4(c). Upon comparing the morphology of the grafted sample [Fig. 4(c)] with ungrafted material [PSy (Fig. 4(a), Na-PCMPsy (Fig. 4(b))] it is clearly evident that the grafted chains have drastically changed the topology of the Na-PCMPsy ($\overline{DS} = 0.13$) sample. As seen from Fig. 4(c), the stiff morphology with adhering characteristics is observed with AN.

V. CONCLUSION

The optimum reaction conditions for photo-induced graft copolymerization of acrylonitrile onto Na-PCMPsy ($\overline{DS} = 0.13$) have been successfully evaluated using UN as a photo-initiator, and the effects of reaction conditions on grafting yields have been studied. Under the optimized reaction conditions, the maximum values of the grafting yields achieved are: %G = 219.62 and %GE = 99.85. The spectral (infrared), XRD and SEM techniques have been used successfully as the evidence of photo-grafting.

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