
Na-PCMTKP-g-PMA: Photo-Induced Synthesis and Characterization

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Abstract

Polymethylacrylate (PMA) grafted Sodium salt of Partially Carboxymethylated Tamarind Kernel Powder (Na-PCMTKP-g-PMA, % G = 260.67, %GE = 92.60) was prepared by photo-grafting of MA onto Na-PCMTKP ($\overline{DS} = 0.15$) using ceric ammonium nitrate (CAN) as a photo-initiator. The optimal reaction condition for affording maximum percentage of grafting were established by varying various reaction parameters. The influence of these reaction parameters on to the grafting yields was also studied. The efficiency of the photo-initiator was investigated by carrying out graft copolymerization of MA onto Na-PCMTKP in the presence and absence of Ultra Violet radiations. The influence of reaction medium on the photo-graft copolymerization was also studied. Photo-grafting process was confirmed and the products were characterized with the help of the spectroscopy (¹H-NMR and FTIR), SEM and thermal (TGA/DSC) techniques.

Keywords: Photo-Initiated grafting, Methyl acrylate, Sodium salt of Partially Carboxymethylated Tamarind Kernel Powder, Optimal Reaction Conditions, Characterization.

INTRODUCTION

The modification of natural and renewable polymers by graft copolymerization process has been widely accepted as an effective method to impart useful properties to the backbone polymer without affecting the original ones. Of the various methods of grafting, photo-initiation using low energy ultraviolet radiation is found to be most promising and practical method because of its simplicity [1].

Tamarind Kernel Powder (TKP), a food grade natural polysaccharide and one of the cheapest gums is derived from the seeds of *Tamarindus indica Linn*; a common and most important tree of

India and South East Asia. The polysaccharide is composed of D-galactose, D-xylose and D-glucose in the molar ratio of 1:2:3[2]. It consists of a main chain of β -D-(1 \rightarrow 4) linked glucopyranosyl units, and a side chain consisting of a single xylopyranosyl unit is attached to every second, third and fourth D-glucopyranosyl unit through a α -D--(1 \rightarrow 6) linkage. One D-galactopyranosyl unit is attached to one of the xylopyranosyl units through a β -D--(1 \rightarrow 2) linkage. TKP has potential commercial applications in textile, explosives, plywood and food industries. Even though TKP finds wide range of industrial applications, it also suffers from some draw backs like biodegradability[3], which limits its uses considerably. These draw backs can be improved through the photo-induced grafting of vinyl monomers onto it. However, due to the low solubility of TKP in cold water, poor solution clarity as well as the desire for products with modified or special properties, we have used carboxymethylated derivative of Tamarind Kernel Powder i.e. Sodium salt of Partially Carboxymethylated Tamarind Kernel Powder (Na-PCMTKP) in the present work for its further modification via photo-induced grafting. The comprehensive literature survey reveals that there is no published report pertaining to the photo-induced grafting of different vinyl monomers onto sodium salt of partially carboxymethylated tamarind kernel powder (Na-PCMTKP) using CAN as a photo-initiator. In the present work we have reported photo-induced grafting of methyl acrylate (MA) onto Na-PCMTKP ($\overline{DS} = 0.15$) using ceric ammonium nitrate (CAN) as a photo-initiator.

EXPERIMENTAL

Material and Methods

Sodium salt of Partially Carboxymethylated Tamarind Kernel Powder (Na-PCMTKP, $\overline{DS} = 0.15$) was kindly supplied by Encore Natural Polymers Ltd; Naroda, Ahmedabad (Gujarat, India). Chiti-chem Corporation, Baroda, Gujarat, India make Methyl acrylate (MA) was washed with 2% sodium hydroxide solution to remove the stabilizer, washed with distilled water, till it was freed from alkali and dried over anhydrous sodium sulphate. Once it free from alkali it was finally distilled at atmospheric pressure and the middle fraction was used. Ceric ammonium nitrate (CAN) of reagent grade (Chiti-chem corporation, Baroda, Gujarat, India) was used as received. All other reagents and solvents used were of reagent grade. Nitrogen gas was purified by passing through fresh pyrogallol solution. Low conductivity water was used for the preparation of all the solutions as well as for polymerization reactions.

Photo-graft Copolymerization

The photo-graft copolymerization reactions were carried out in a photochemical reactor (Figure 1) supplied by Scientific Aids and Instruments Corp. (SAIC, Madras, India) as per the procedure described as under : A weighed amount of Na-PCMTKP ($\overline{DS} = 0.15$, 0.5 to 3.0 g, dry basis) was dissolved in 146 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 half an hour at 55°C and there after 20 mins 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 reaction flask, and the contents were then flushed with purified nitrogen gas for half an hour, followed by

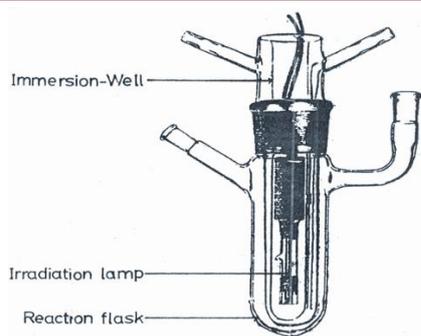
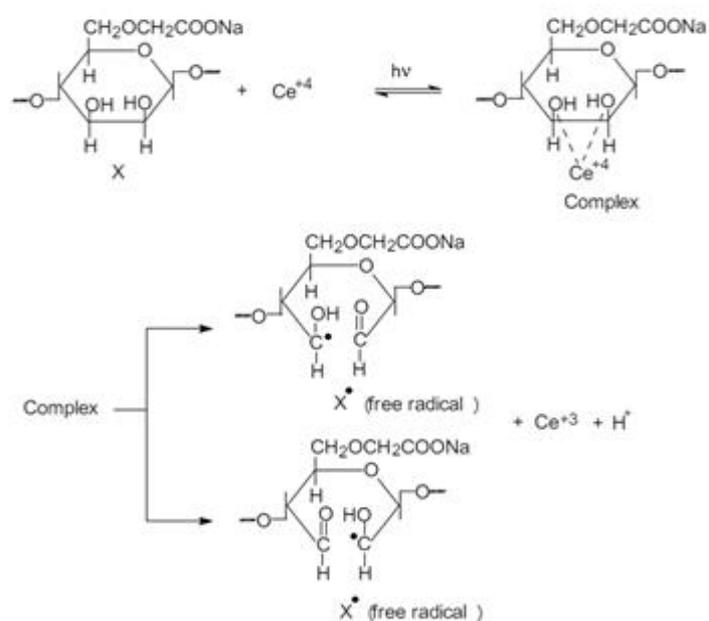
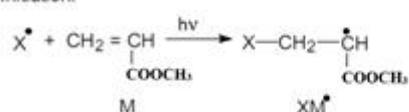


Figure 1: Photochemical reactor

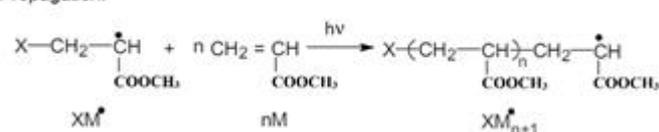
Radical Generation:



Initiation:



Propagation:



Termination:

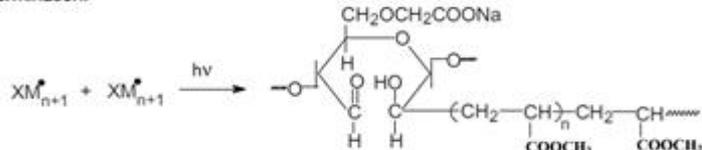


Figure 2: Mechanistic pathway for the synthesis of Na-PCMTKP-g-PMA

the addition of a known concentration of freshly distilled MA (0.037 – 0.369 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 (0.5-10h) in the temperature range of 20-45°C. After the completion of the photo-grafting reaction, the irradiated sample solution was removed carefully, and the crude graft copolymer was isolated by centrifugation. It was then purified by repeated washings with 95% methanol and finally with pure methanol. The crude copolymer sample of Na-PCMTKP-g-PMA thus obtained was dried in vacuum oven at 40°C. The homopolymer (PMA) was separated from the crude graft copolymer by carrying out exhaustive soxhlet extraction with acetone. After the complete removal of the homopolymer, the pure graft copolymer was dried at 40°C in vacuum until a constant weight was obtained. The mechanistic pathway for the synthesis of the graft copolymer, Na-PCMTKP-g-PMA, is shown in Figure-2.

Dark Method

To compare the efficiency of CAN as a photo-initiator, the grafting of MA onto Na-PCMTKP ($\overline{DS} = 0.15$) was carried out in the absence of ultraviolet radiation (dark method) by following the above mentioned procedure using the following reaction conditions: Na-PCMTKP = 1.50g (dry basis); [CAN] = 1.0×10^{-3} mol/L; [HNO₃] = 0.1mol/L; [MA] = 0.111 mol/L; Time = 0.5h to 10h; Temperature = 35°C; Volume of water = 145.50 mL and Total Volume = 150 mL.

Effects of Reaction Medium on Photo-grafting

In the present case, the evaluated optimal reaction conditions were used to study the effects of reaction medium. The photo-graft copolymerization reactions, were carried out exactly in the similar manner as described above. The selected ratio (%V/V) of water to organic solvent was in the proportion of 100:Nil, 75:25, 50:50 and 25:75. The organic solvents used were methanol, ethanol, n-propanol and n-butanol. After completion of reaction medium, the crude graft copolymers were isolated and purified as discussed above. The crude graft copolymer samples containing MA, thus obtained, were dried in a vacuum oven at 40°C.

Isolation of Grafted Chains

The graft copolymer of Na-PCMTKP ($\overline{DS} = 0.15$) containing PMA was hydrolyzed by refluxing for 12 h in 1N HCl as suggested by Brockway and Seaberg[4]. After all the Na-PCMTKP went into the solution, a resinous mass was obtained which was characterized with IR spectroscopy.

FTIR Spectra

The IR Spectra of Na-PCMTKP ($\overline{DS} = 0.15$), Na-PCMTKP-g-PMA and PMA were taken in KBR pellets using Nicolet Impact 400D Fourier Transform Infrared Spectrophotometer.

¹H-NMR Spectra

¹H-NMR spectrum of the grafted chains i.e. PMA obtained after acid hydrolysis of the graft copolymer (Na-PCMTKP-g-PMA) was recorded on a fourier transform NMR spectrometer (Bruker Avance 400 spectrometer) with CDCl₃ as the solvent.

Thermogravimetric Analysis (TGA)

The thermal behaviour of Na-PCMTKP ($\overline{DS} = 0.15$), Na-PCMTKP-g-PMA and PMA were examined in an inert atmosphere at a heating rate of 10°C/min with the help of Dupont 951 thermogravimetric analyzer.

Differential Scanning Calorimetry (DSC)

The DSC scans of Na-PCMTKP ($\overline{DS} = 15$) and Na-PCMTKP-g-PMA were recorded in nitrogen atmosphere at a scan rate of 10°C/min on DSC 2920 TA instrument.

Scanning Electron Microscopy (SEM)

Model ESEM TMP + EDAX, Philips make was used to obtain the micrographs of Na-PCMTKP ($\overline{DS} = 0.15$) and Na-PCMTKP-g-PMA (% G = 260.67).

Grafting yields:

The grafting yields viz. percent grafting(%G) and grafting efficiency (%GE) by the help of the following expressions:

$$\% G = \frac{\text{Wt. of Polymer Grafted}}{\text{Initial Wt. of backbone}} \times 100 \quad (1)$$

$$\% GE = \frac{\text{Wt. of Polymer Grafted}}{\text{Wt. of Polymer Grafted} + \text{Wt. of Homopolyme r}} \times 100 \quad (2)$$

RESULTS AND DISCUSSION

In order to gain an insight into the mechanism of the photo-grafting reaction, the effect of variables in the synthesis such as amount of substrate, concentrations of photo-initiator, nitric acid and monomer as well as time and temperature were studied.

Effect of backbone concentration

Figure 3(a) shows the influence of varying amount of Na-PCMTKP on the grafting yields. It is seen from this figure that with increasing Na-PCMTKP concentration, %G decreases steadily but %GE increases up to the optimum concentration of the backbone Na-PCMTKP = 1.5 gm thereafter it is found to be leveled off with further increase in amount of Na-PCMTKP. The observed increase in % GE with an increase in the amount of Na-PCMTKP is due to the increase in the weight of the grafted side chains. The descending trend in % G is attributed to the high

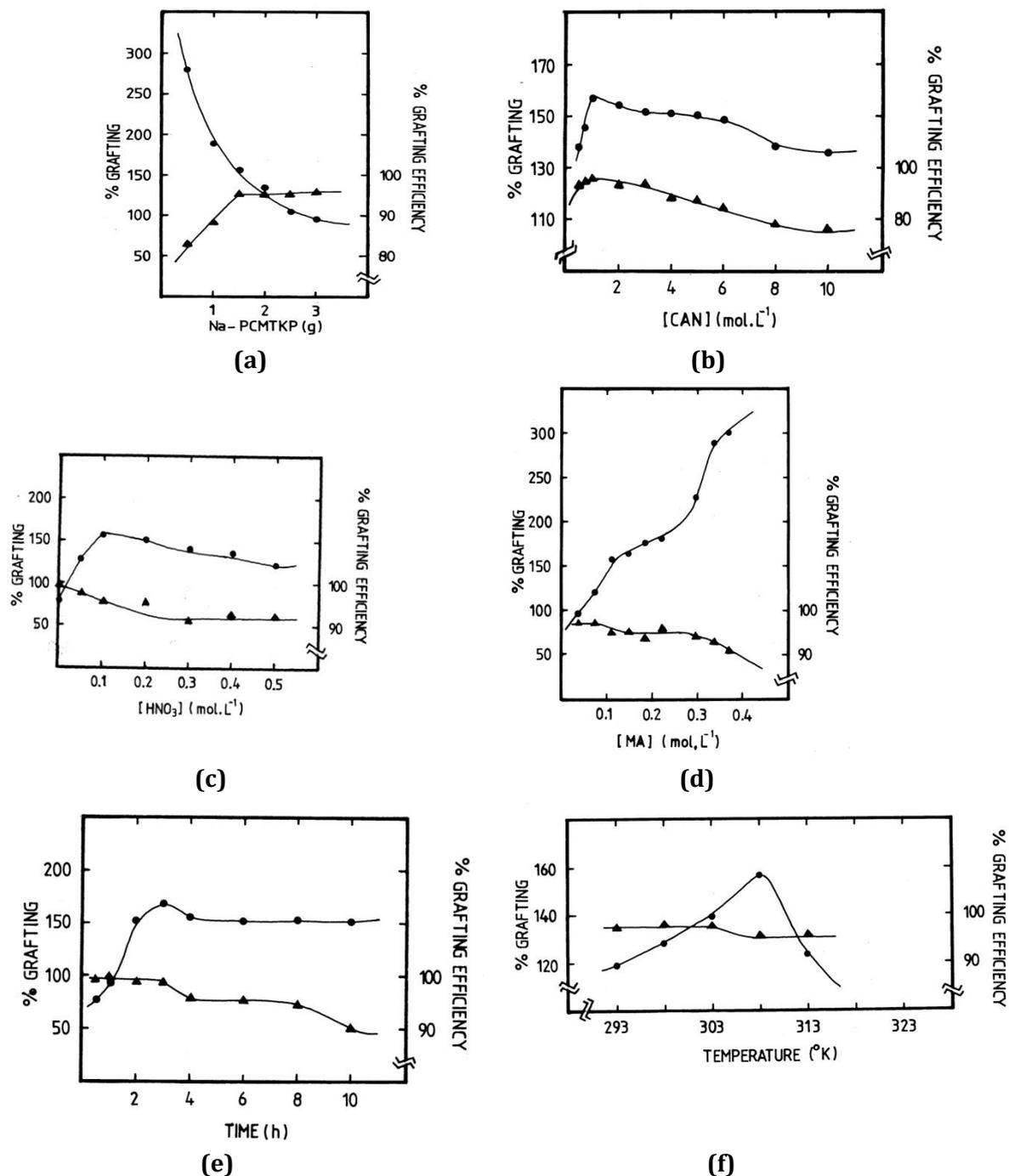


Figure 3: Influence of (a) amount of sodium salt of partially carboxymethylated Tamarind Kernel Powder (Na-PCMTKP); (b) Ceric Ammonium Nitrate (CAN) concentration; (c) nitric acid concentration; (d) methyl methacrylate (MMA) concentration; (e) reaction time and (f) reaction temperature on: (●) - %G; or (▲) - %GE.

viscosity of Na-PCMTKP solution. With increase in concentration of Na-PCMTKP, the viscous reaction medium has made the diffusion of both monomer and the photo-initiator near to Na-PCMTKP more difficult, thereby greatly hindering the rate of photo-graft copolymerization. In

addition, the decrease in the monomer-to-backbone ratio also accounted for the observed decrease in %G. Similar observations have also been reported earlier[5-8].

Effect of photo-initiator concentration

The effect of the photo-initiator (CAN) concentration on photo-graft copolymerization was studied by varying the concentration of CAN from 0.5×10^{-3} to 10.0×10^{-3} mol/L. The results are presented in Figure 3(b). It is seen from this figure that initially both %G and %GE are found to be increased with increase in photo-initiator concentration reaching maximum values of %G = 188.06 and %GE = 88.58 at $[CAN] = 1.00 \times 10^{-3}$ mol/L. Beyond optimum value of the photoinitiator concentration both %G and %GE are found to be decreased. The increasing trend in the grafting yields (%G and %GE) is attributed to the fact that within the photo-initiator concentration range (0.5×10^{-3} mol/L - 1.00×10^{-3} mol/L) the complex formation between -OH groups as well as carboxylate anion of Na-PCMTKP and Ce^{4+} is facilitated and the photodecomposition of the complex gives more and more active sites. Thus, this activation along the backbone which has taken place is immediately followed by the photo-graft copolymerization of MA onto Na-PCMTKP backbone. The observed decrease in grafting yields (%G and %GE) may be attributed to the fast termination of the growing grafted chains. Furthermore, homopolymer (PMA) formation at higher initiator concentration which competes with the grafting reaction for the available monomer (MA) could also lead to a decrease in % G as well as % GE. Similar results are also reported in the literature [9-12].

Effect of acid concentration

The influence of the HNO_3 concentration on the grafting yields was studied by varying the acid concentration in the range nil-0.5 mol/L and the results are depicted in Figure 3(C). It is evident from the figure that there exists an optimum concentration of nitric acid (0.10 mol/L) to provide maximum %G (156.92%). Beyond the optimum concentration of nitric acid, the value of %G is found to be decreased. However, even at zero concentration of nitric acid, the value of %G is found to be 78.98% [cf. Figure 3(c)] which is due to the possibility that, even in the absence of acid, Na-PCMTKP ionizes to a greater extent in an aqueous medium, thereby facilitating the diffusion of monomer as well as photo-initiator leading to a higher value of grafting yields. Below the optimum concentration, the observed increase in the value of %G with increase in the nitric acid concentration is attributed to an increase in the initiation rate of photo-grafting. However, at higher acid concentrations, the observed decrease in the %G and %GE could be due to a corresponding reduction in ceric-Na-PCMTKP complex formation as well as an increase in polymer termination rates. Similar results are also reported elsewhere [9, 10, 13].

Effect of monomer concentration

Figure 3(d) shows the influence of the monomer (MA) concentration on %G and %GE. The value of %G increases steadily in the beginning up to 0.111 mol/L, beyond which the value of %G increases slowly. The further continuous increase in %G, upon increasing the monomer concentration as observed in this figure could be attributed to variety of reasons: the first reason is that the complexation of Na-PCMTKP with monomer, which is required for monomer reactivity, would be favored with increase in monomer concentration; the second reason might be due to the gel effect i.e. increase in viscosity of the medium owing to the solubility of the homopolymer

(PMA) in its own monomer (MA) which could be more pronounced with increase of monomer concentration. On the other hand, the value of %GE is found to decrease with increasing monomer concentration showing 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 (MA) into the backbone. As a result of which less monomer would be available for photo-grafting and most of it may be used for homopolymerization. Similar observations have also been reported in the literature[7, 9, 14-18].

Effect of reaction time

Grafting reaction was also studied by varying the time period from 0.5h to 10h and the results are depicted in Figure 3(e). It becomes evident from this figure that the value of %G increases in the beginning and reaches the maximum value 163.23% at 3h. However, the value of %GE remains almost constant up to 3h beyond which %GE decreases with further increase in time. The observed increase in %G 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 reaction time leading to the increase in %G. But beyond the optimum value of reaction time i.e. 3h, as the available sites for photo-grafting of MA onto Na-PCMTKP backbone get reduced and thereby decreasing both the values of %G and %GE. Similar results are also reported in the literature[19,20].

Effect of temperature

In order to study the influence of temperature on the grafting yields, photo-grafting reactions were carried out at six different temperatures, ranging from 20-45°C. The results are presented in Figure 3(f). It can be seen from the figure that the value of %G is found to be increased up to 35°C. Beyond which, the value of %G decreases but the value of %GE remains steady. The increase in %G could be interpreted in terms of favourable influence of temperature on : (a) the faster photolysis of Na-PCMTKP-Ceric complex so that more active sites are generated on the Na-PCMTKP chains; (b) the swellability of Na-PCMTKP; (c) solubility of monomer (MA) molecules; (d) diffusion rate of monomer from the aqueous phase to the backbone; and (e) the rates of initiation and propagation of photo-grafting. The observed decrease in %GE with rising temperature may be attributed to the solubility of monomer in the aqueous phase at the higher temperatures, thus increasing the possibility of the monomer to contact Ce(IV), hence more Ce(IV) might be available to initiate the homopolymerization. Besides, at higher temperature various hydrogen abstraction and chain transfer reactions might be accelerated which lead to decrease in %G as well as %GE. Similar results are also reported by earlier researchers [9, 16, 21, 22].

From the above, the optimized reaction conditions evaluated in the present study of photo-graft copolymerization of MA onto Na-PCMTKP are: Na-PCMTKP = 1.5g (dry basis); [CAN] = 1.0×10^{-3} mol/L; [HNO₃] = 0.10 mol/L; [MA] = 0.295 mol/L; Time = 3h; Temperature = 35°C, Volume of Water = 143.50 mL and Total Volume = 150 mL. The maximum values of the grafting yields achieved are % G = 260.67 and % GE = 92.60.

Effect of Reaction Medium :

The photo-grafting of methyl acrylate (MA) onto Na-PCMTKP ($\overline{DS}=0.15$) using CAN as a photoinitiator was studied in different water/solvent mixtures. The solvents used include methanol, ethanol, n-propanol and n-butanol. The results obtained are summarized in Table 1. It can be revealed from Table 1 that regardless of the water/solvent mixture employed, a substantial amount of grafting is obtained. A regular decrease in %grafting occurs with increasing the solvent ratio in the water/solvent mixture. This could be interpreted in terms of

Table 1. Influence of reaction medium on photo-graft copolymerization of methylacrylate (MA) onto (Na-PCMTKP, $\overline{DS} = 0.15$) using ceric ammonium nitrate (CAN) as a photoinitiator^a.

Solvent	Water/Solvent Ratio (V/V)	%Grafting (%G)	%Grafting Efficiency (%GE)
Methanol	100:00	260.67	92.60
	75:25	184.45	74.17
	50:50	100.01	93.12
	25:75	89.24	92.63
Ethanol	100:00	260.67	92.60
	75:25	116.34	47.36
	50:50	93.44	74.80
	25:75	80.07	89.07
n-Propanol	100:00	260.67	92.60
	75:25	106.25	74.98
	50:50	88.16	91.82
	25:75	83.81	92.91
n-Butanol	100:00	260.67	92.60
	75:25	97.17	86.27
	50:50	82.60	91.99
	25:75	74.47	84.64

^a**Reaction conditions :** [Na-PCMTKP] = 1.5 g (dry basis); [CAN] = 1.0×10^{-3} mol/L; [HNO₃]=0.10 mol/L; [MA] = 0.332 mol/L; Reaction Time = 3.0 h; Temperature = 35°C; Volume of water =143.50 mL and Total Volume = 150mL

substantial amount of grafting is obtained. A regular decrease in %grafting occurs with increasing the solvent ratio in the water/solvent mixture. This could be interpreted in terms of the adverse effect of the solvent on the swelling properties of Na-PCMTKP in water. It becomes further evident upon inspection of the results of the Table that the reaction medium plays an important role in photo-graft copolymerization reaction. The magnitude of grafting differs significantly with the type and ratio of solvent used in the mixture. The graft yield follows the order : Methanol > Ethanol > n-Propanol > n-Butanol when the solvent constitutes either 25% or 50% in the water/solvent mixtures. On the other hand when the solvent constitutes 75% in the water/solvent mixture, the graft yield follows the order: Methanol > n-Propanol > Ethanol > n-Butanol. Further, it is important to note from the results that of the water/solvent mixtures used, water/methanol at a ratio of 75/25 constitutes the most favorable medium for photo-graft polymerization of MA with Na-PCMTKP ($\overline{DS} = 0.15$) using CAN as a photo-initiator giving rise to highest value of %G. This can be attributed to the small molecule of methyl alcohol and also to its high polarity, which is not only capable of swelling the trunk polymer but also has the additional advantage of being miscible with the monomer, thus simplifying the access and diffusion to the grafting sites in the Na-PCMTKP. Differences in % grafting obtained with water/solvent mixtures as polymerization medium could be attributed to differences in (i) miscibility with monomer (MA), (ii) ability to swell Na-PCMTKP, (iii) compatibility with the CAN, and (iv) termination of the graft chain radical and Na-PCMTKP macroradical via. chain transfer. While the first three factors enhance grafting by simplifying the access and diffusion of the monomer, the last factor adversely effects grafting by lowering the molecular size of the graft. Similar results are also reported earlier [23-25].

Comparison of Efficiency of CAN

In order to compare the efficiency of CAN as a photo-initiator in the presence as well as absence of the ultra-violet radiation, photo-grafting of MA onto Na-PCMTKP at various reaction timings was carried out and the results of the %G obtained by following photo and dark methods are depicted in Figure 4. It becomes evident from this figure that the values of %G are higher when

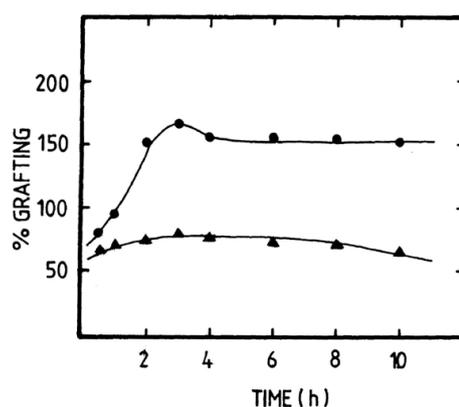


Figure 4: Effect of reaction time on % G : (●) - photo method ; and (▲)- dark method grafting of MA has been carried out onto Na-PCMTKP at various reaction times using ultraviolet radiation in comparison with the dark method. The reason for the observed higher values of %G may be attributed to the fact that the complex, which has been formed by the reaction between the functional groups of Na-PCMTKP and Ceric ions, may dissociate to a greater extent in the presence of ultra-violet radiation (photo-method) than in comparison with absence of radiation

(dark-method). As a result of which greater number of free radical sites may be produced for grafting to occur in photo-method leading to higher values of %G.

Evidence of Grafting

(a) FTIR Spectra:

Figure 5 shows the IR spectrum of Na-PCMTKP ($\overline{DS} = 0.15$). The presence of a very strong and broad absorption band at $\sim 3435 \text{ cm}^{-1}$ is assigned to $-\text{OH}$ stretching. Reasonably sharp absorption band at $\sim 2925 \text{ cm}^{-1}$ may be attributed to the $-\text{CH}$ stretching. The asymmetric and symmetric vibrations due to $-\text{COO}^-$ moiety are assigned to $\sim 1662 \text{ cm}^{-1}$ and $\sim 1420 \text{ cm}^{-1}$ respectively. This can be attributed to the incorporation of carboxymethyl groups in Tamarind Kernel Powder.

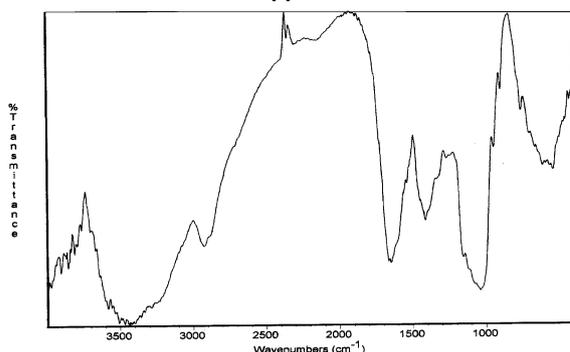


Figure 5: IR spectrum of Sodium salt of Partially Carboxymethylated Tamarind Kernel Powder (Na-PCMTKP, $\overline{DS}=0.15$) sample

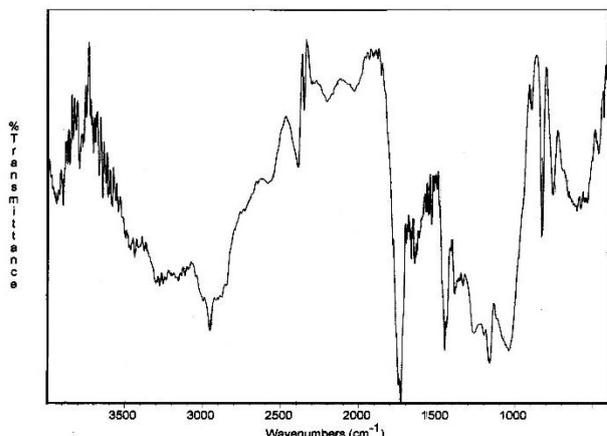


Figure 6: IR spectrum of Na-PCMTKP-g-PMA (%G = 260.67) sample.

The IR spectra of the graft copolymer Na-PCMTKP-g-PMA (Figure 6), showed absorption bands of Na-PCMTKP as well as an additional strong absorption band at about $1730\text{-}1750 \text{ cm}^{-1}$ assigned to $\text{C}=\text{O}$ stretching of ester group ($-\text{COOCH}_3$), characteristic of methacrylates.

The IR spectrum of PMA (Figure 7) indicates the presence of $\text{C}=\text{O}$ stretching at about $1730\text{-}1750 \text{ cm}^{-1}$. This may be attributed to the fact that hydrolysis of the graft copolymer, Na-PCMTKP-g-PMA, gives back methyl acrylates. Thus, the results of Figures 5-7 provide a substantial evidence of grafting of MA onto Na-PCMTKP ($\overline{DS} = 0.15$).

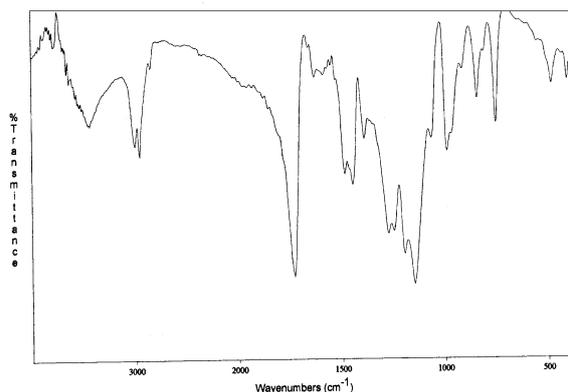


Figure 7: IR Spectrum of PMA sample.

(b)¹H- NMR spectra of isolated grafted chains :

The graft copolymer sample viz. Na-PCMTKP-g-PMA was hydrolyzed and the ¹H-NMR of the corresponding hydrolyzed product i.e. PMA was recorded.

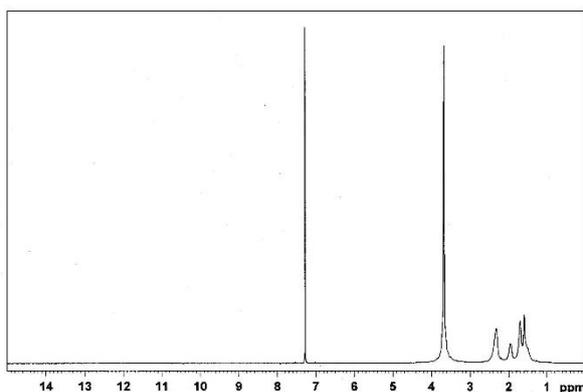


Figure 8: ¹H - NMR spectrum of polymethyl acrylate (PMA) sample

The following peaks are observed from the ¹H-NMR spectrum of PMA (Figure 8) and their assignment is as under :

<u>Peak</u>	<u>Assignment</u>
1.95 δ	-CH ₂
2.33 δ	-CH
3.68 δ	-OCH ₃

The - CH₂ resonance has been assigned around 2.0 δ . The CH₃ of -OCH₃ is attributed to the peak in the region 3.6-3.8 δ , while CH₃ in C-CH₃ appears around 1.0 δ . Thus, the results of ¹H-NMR (Figure 8) support the data obtained from IR studies thereby testifying to the existence of grafting of MA onto Na-PCMTKP ($\overline{DS} = 0.15$).

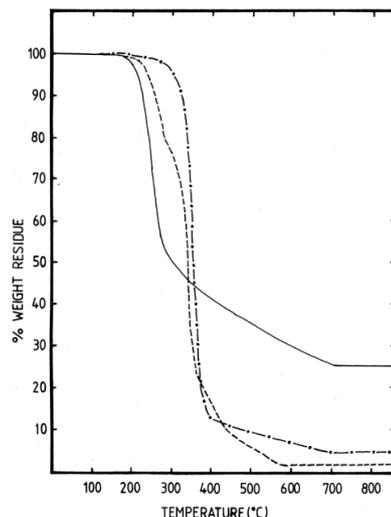
(c) Thermogravimetric Analysis (TGA) :

Figure 9: TG thermogram for (—) Na-PCMTKP ($\overline{DS} = 0.15$), (-----); Na-PCMTKP-g-PMA (%G = 260.67) and (— ● — ● —) PMA at 10°C/min

The primary thermograms obtained at a scan rate of 10°C/min for Na-PCMTKP ($\overline{DS} = 0.15$), Na-PCMTKP-g-PMA (% G = 260.67) and PMA in an inert atmosphere are shown in Figure 9. In the samples, about 5-10 % loss in weight was observed below 100°C. This was attributed to absorbed water and has not been taken into consideration while plotting the weight residue versus temperature curves. The overall degradation of Sodium salt of Partially Carboxymethylated Tamarind Kernel Powder, Na-PCMTKP ($\overline{DS} = 0.15$) involves only single step. The sample begins to decompose at 160°C, rapidly loses 47.5 % of its weight up to 280°C. Beyond 280°C, the weight loss is slow and gradual up to about 700°C leaving 25.5 % residual weight. In the temperature range 280-700°C, the sample loses 28 % of its original weight. The maximum rate of weight loss occurs at 260°C. The overall thermal degradation of Na-PCMTKP-g-PMA exhibits two steps. The sample begins to decompose at about 140°C and loses its weight very slowly up to 285°C involving about 21 % weight loss. The second decomposition step is immediately followed and marked with a rapid weight loss in a temperature range 300-350°C during which the graft copolymer sample loses 46 % of its weight. Beyond 350°C, the degradation is found to proceed with a slow rate up to 580 °C leaving behind 2% weight residue. The maximum rates of weight loss for the first and second decomposition steps are 260°C and 330°C respectively. In the case of PMA, the overall degradation also involves only single step which commences from 195°C and completes at about 700°C, involving about 95 % weight loss with a maximum rate of weight loss 350°C. A char yield of only 5 % is obtained.

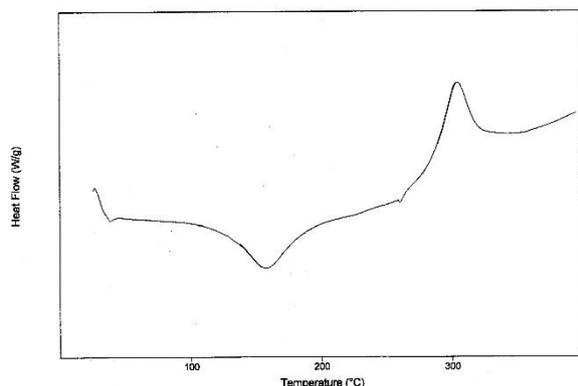
(d) Differential Scanning Calorimetry (DSC):

Figure 10: Differential Scanning Calorimetric (DSC) scan for Na-PCMTKP ($\overline{DS} = 0.15$) at a heating rate of 10°C/min in nitrogen atmosphere

Figure 10 represents the DSC scan of Na-PCMTKP ($\overline{DS}=0.15$) sample. The endothermic transition appeared at 157.43°C is due to the melting of Na-PCMTKP but the exothermic transition observed at 303.88°C is attributed to the decomposition of the sample.

The DSC scan of Na-PCMTKP-g-PMA (Figure 11) shows the broad narrow endothermic transition at 177.21°C which may be due to the gross melting of the graft copolymer sample. The exothermic peak observed at 314.68°C is due to the gross decomposition of the graft copolymer sample containing PMA.

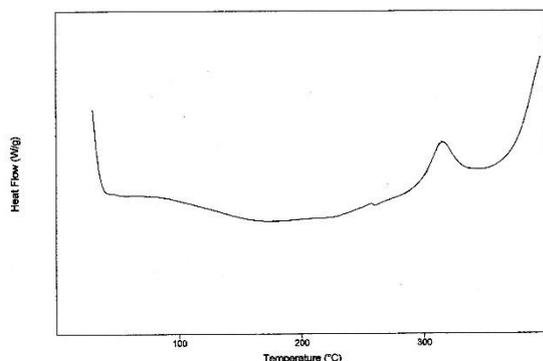


Figure 11: Differential Scanning Calorimetric (DSC) scan for Na-PCMTKP-g-PMA (%G = 260.67) at a heating rate of 10°C/min in nitrogen atmosphere

Thus, from the above figures it is evident that in the case photo-grafting of MA onto Na-PCMTKP ($\overline{DS}=0.15$), the Na-PCMTKP decomposition peak (303.88 °C cf. in Figure 10) was found to be shifted to the higher temperature of 314.68 °C in the case of Na-PCMTKP-g-PMA (Figure 11) which indicated the almost simultaneous decomposition of grafted polymer chains (PMA) and the decomposition of Na-PCMTKP ($\overline{DS}=0.15$).

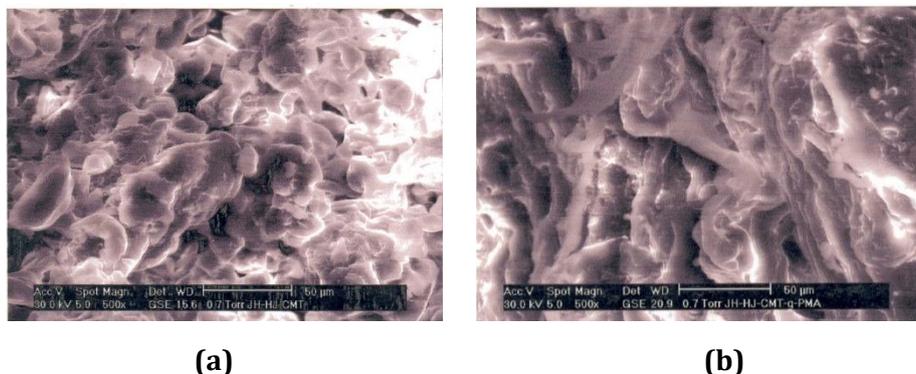
(e) Scanning Electron Microscopy (SEM):

Figure 12: Scanning Electron Micrographs of (a) Na-PCMTKP (500X) and (b) Na-PCMTKP-g-PMA (%G = 260.67) (500X).

Figures 12(a) and 12(b) represent the scanning electron micrographs of Na-PCMTKP and Na-PCMTKP-g-PMA respectively. The comparison of the micrographs led to revealed that the grafted chains have drastically changed the topology of Na-PCMTKP sample. As seen in Figure 12(b) the lumpy morphology is observed indicating that photo-grafting of MA onto Na-PCMTKP has taken place.

Conclusions

In the present work, an unreported photo-initiated graft copolymerization of MA onto Na-PCMTKP ($DS=0.15$) has been studied using CAN as a photo-initiator. The influence of reaction variables such as concentrations of photo-initiator (CAN), nitric acid and monomer (MA) as well as reaction time, temperature and amount of substrate on the grafting yields has been studied and the optimal reaction conditions have been evaluated. Under the optimal reaction conditions, the maximum values of the grafting yields achieved are %G = 260.67 and %GE = 92.60. The efficiency of the photo-initiator CAN has been studied by carrying out photo-graft copolymerization of MA onto Na-PCMTKP in the presence and absence of ultraviolet radiations. The evaluated optimal reaction conditions have been also utilized to study the effect of reaction medium on the photo-grafting. It has been observed that the reaction medium plays an important role in photo-graft copolymerization reaction and the magnitude of grafting differs significantly with the type and ratio of solvent used in the mixture. The evidence of photo-grafting has been ascertained by spectral (1H -NMR and FTIR), SEM and thermal (TGA/DSC) techniques. The synthesized graft copolymer, Na-PCMTKP-g-PMA, after treating it with hydroxylamine in the alkaline medium may find its potential applications as an adsorbent for metal ion sorption. Further work in this regard is in progress.

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