



Synthesis and Characterization of Poly(methyl acrylate)-grafted-Sodium Salt of Partially Carboxymethylated Tamarind Kernel Powder

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Ceric ammonium nitrate (CAN)-initiated graft copolymerization of methyl acrylate (MA) onto sodium salt of partially carboxymethylated tamarind kernel powder (Na-PCMTKP, $\overline{DS} = 0.15$) was studied in an aqueous medium by solution polymerization technique. The growth of the graft reaction was monitored gravimetrically. The role of various synthesis variables on the grafting yields was examined to achieve the maximum graft yields (%G = 278.27, %GE = 94.38, %Hp = 5.62) and the influence of the synthesis variables in the graft copolymerization has been discussed. The reactivity of methyl acrylate (MA) towards graft copolymerization was compared with that of acrylonitrile (AN) on the basis of the results obtained from the earlier studies and plausible explanation was furnished for the observed reactivity of both the monomers towards grafting. The evaluated optimized reaction conditions were utilized to study the effect of reaction medium on grafting and it was found that reaction medium plays an important role in graft copolymerization. In order to ascertain the grafting, characterization of the samples made by FTIR, TGA and SEM was conducted. The synthesized novel graft copolymer may find potential application to be used as metal adsorbents.

Keywords: Sodium salt, Carboxymethylated tamarind kernel powder, Methyl acrylate, Ceric-initiated, Graft copolymerization.

INTRODUCTION

As graft copolymerization is a versatile tool, the considerable interest has been provoked on chemical modification of polysaccharides through grafting employing chemical as well as radiation techniques [1,2]. Tamarind kernel powder (TKP), a highly branched neutral, non-ionic polysaccharide with considerably high molecular weight, is composed of D-galactose, D-xylose and D-glucose in the molar ratio of 1:2:3 [3]. It is composed of main chain of β -D-(1 \rightarrow 4) linked glucopyranosyl units and that 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 [3,4]. Although, TKP (Fig. 1) is the cheapest gum and is known for its wide range of food

and non-food industrial applications [5], it is having several drawbacks [4] such as unpleasant odour due to fat (7%), dull color, presence of water insoluble ingredients and low solubility in cold water. In order to overcome these drawbacks, molecular modification of TKP is required to be carried out. In addition, TKP is having advantages like it is biocompatible and non-carcinogenic in nature but it has an additional disadvantage like biodegradability [6], which limits its uses considerably. However, this drawback can also be improved by carrying out the modification of TKP and its derivatives through grafting, thereby imparting new characteristic properties to the polymer backbone.

In present study, the carboxymethylated derivative of TKP (Na-PCMTKP, $\overline{DS} = 0.15$) was used and further graft copolymerized with methyl acrylate with an aim to develop a product, which could be used as metal adsorbents by treating it with

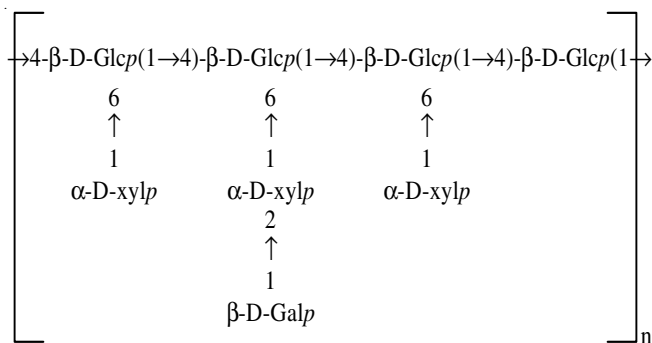


Fig. 1 Structure of tamarind kernel powder (TKP)

hydroxylamine in the presence of alkaline solution. The presence of carboxymethyl groups in the TKP will make the polymer anionic and improve the hydration of TKP as a result of which the diffusion monomer (MA) and the initiator ceric ammonium nitrate (CAN) will get facilitated leading to the enhancement in the reactivity of TKP toward grafting.

The literature survey reveals that the graft copolymerization of acrylamide [7], acrylonitrile [8] and hydroxymethacrylate [9] has been carried out onto carboxymethyl tamarind kernel powder (CMTKP) using chemical and microwave assisted methods. However, we have modified sodium salt of partially carboxymethylated tamarind kernel powder (Na-PCMTKP, $\overline{DS} = 0.15$) through grafting with acrylonitrile [10] using CAN as a redox initiator and the optimally synthesized hydrophobic graft copolymer, Na-PCMTKP-*g*-PAN ($\%G = 413.76$, $\%GE = 96.48$) was completely converted into a hydrophilic gel *i.e.* a superabsorbent hydrogel (H-Na-PCMTKP-*g*-PAN) with high water absorption capacity through its alkaline hydrolysis (0.7N KOH solution at 90-95 °C) [11]. In continuation of this work, a systematic study of the grafting of methyl acrylate (MA) onto Na-PCMTKP ($\overline{DS} = 0.15$) is conducted, taking into account all synthesis variables in an orthogonal experimental grid, to finally arrive at optimal synthesis conditions and a proof that the optimized product is indeed grafted in terms of its characterization.

EXPERIMENTAL

Sodium salt of partially carboxymethylated tamarind kernel powder (Na-PCMTKP, $\overline{DS} = 0.15$) was obtained from Encore Natural Polymers Ltd., (India). Methyl acrylate (MA) (Chiti-Chem Corporation, India) was washed with 2% NaOH solution to remove the stabilizer, washed with distilled water till it was freed from alkali and dried over anhydrous sodium sulphate and was purified by carrying out its distillation. Ceric ammonium nitrate (CAN) of reagent grade was procured from Chiti-Chem Corporation (India) and was used as received. All other chemicals of reagent grade were used as such. The solvents used in the present work were also purified prior to their use. Nitrogen gas was purified by passing through fresh pyrogallol solution. In the preparation of all the solutions as well as for polymerization reactions, low conductivity water was used.

Synthesis of Na-PCMTKP-*g*-poly(methyl acrylate):

The graft copolymer, Na-PCMTKP-*g*-PMA, was synthesized as per the procedure described earlier [10]. However, the reaction

conditions which were varied, in the present study, for establishing the optimal reaction conditions are: weight of Na-PCMTKP: 0.5 to 3.0 g (dry basis); [CAN]: 2.5×10^{-3} to 80×10^{-3} mol L⁻¹; [HNO₃]: Nil to 1.0 mol L⁻¹; [MA]: 0.037 to 0.370 mol L⁻¹; Reaction time: 0.5-10 h; Temperature: 15 to 55 °C and Total volume: 150 mL.

The resultant crude graft copolymer, after completion of the reaction, was precipitated out with excess of methanol. After filtration of the copolymer product, it was washed repeatedly with nitric acid, 90% methanol and finally with pure methanol. Precipitated crude graft copolymer was finally dried under vacuum at 40 °C. The resulting crude graft product was Soxhlet extracted with acetone for 48 h to extract the homopolymer, *i.e.* poly(methyl acrylate). Thus, the pure graft copolymer (Na-PCMTKP-*g*-PMA) obtained was dried at 40 °C under vacuum. The graft copolymer sample was hydrolyzed by refluxing it for 12 h in 1.0 mol L⁻¹ HCl, as suggested by Brockway [12], for isolation of the grafted PMA chains.

Grafting yields and rate of polymerization: The following equations were used to calculate the grafting yields [percentage of grafting (%G), percentage of grafting efficiency (%GE) and percentage of homopolymer (%Hp)] and the rate of polymerization [10]:

$$G (\%) = \frac{\text{Wt. of polymer grafted}}{\text{Initial wt. of Na-PCMTKP}} \times 100 \quad (1)$$

$$GE (\%) = \frac{\text{Wt. of polymer grafted}}{\text{Wt. of polymer grafted} + \text{Wt. of homopolymer}} \times 100 \quad (2)$$

$$\%H_p = 100 - \%GE \quad (3)$$

$$R_p (\text{mol L}^{-1} \text{ s}^{-1}) = \frac{\text{Polymer weight} + \text{Homopolymer weight}}{\text{Monomer (m.w.)} \times \text{Reaction time} \times \text{Reaction mixture volume}} \times 10^3 \quad (4)$$

Reaction medium and grafting: The influence of reaction medium in the case of grafting of MA onto Na-PCMTKP ($\overline{DS} = 0.15$) was studied by using the evaluated optimized reaction conditions. The organic solvents used *viz.* methanol, ethanol, *n*-propanol and *n*-butanol. The selected water/solvent ratio (%v/v) was in the proportion of 100:nil, 75:25, 50:50, 25:75 and Nil:100. The graft copolymerization reactions were performed by following the same procedure as described above. The methods of isolation and the purification of the graft copolymer were also the same as described above.

FTIR analysis: The Nicolet impact 400D Fourier transform infrared spectrophotometer was used to record the FTIR spectra of Na-PCMTKP ($\overline{DS} = 0.15$), Na-PCMTKP-*g*-PMA ($\%G = 278.27$) and PMA using KBr pellet method.

Thermal analysis: A DuPont 951 thermal analyzer was used to perform thermogravimetric analysis (TGA) of Na-PCMTKP ($\overline{DS} = 0.15$), its graft copolymer containing PMA (Na-PCMTKP-*g*-PMA, $\%G = 278.27$) and the homopolymer (PMA) samples. The samples were heated at a rate of 10 °C/min from room temperature up to 700 °C under nitrogen atmosphere.

Scanning electron microscopy (SEM) analysis: The surface structure and morphology of Na-PCMTKP ($\overline{DS} = 0.15$)

and graft copolymer (Na-PCMTKP-g-PMA, %G = 278.27) samples were examined by using Model ESEM TMP + EDAX (Philips make) at 500 magnification. The accelerating voltage was 30 kV with the secondary electron image as a detector.

RESULTS AND DISCUSSION

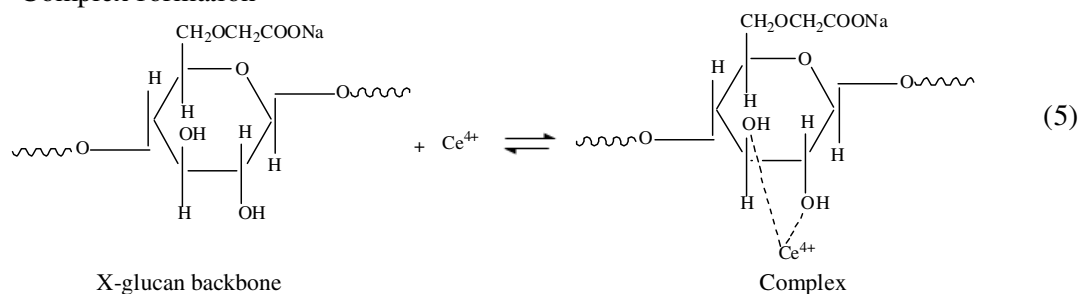
Mechanism of grafting: A reaction scheme (Fig. 2) has been proposed to elucidate in brief about the mechanism of grafting of methyl acrylate (MA) onto Na-PCMTKP ($\overline{DS} = 0.15$) initiated by Ce(IV) ion in an aqueous medium. The Ce(IV) ion in acidic solution forms a most stable chelate complex with glucopyranosyl unit of the Na-PCMTKP molecule, probably by reaction through the hydroxyl groups on carbon C₂ and C₃ (eqn. 5). As a result of one electron transfer reaction, the Ce(IV) is reduced to Ce(III) ions, followed by the release of Ce(III) ions and anhydroglucose ring cleavage at the C₂-C₃ bond, leading to the formation of a short-lived free radical on either carbon C₂ or C₃ (eqn. 6). Thus, these reactive macro-radicals in the presence of the monomer (MA) molecules, generate Na-PCMTKP-g-PMA, graft copolymer (eqn. 7). Thus, as mentioned above in the present case the grafting occurs mainly at the C₂-C₃ position.

Influence of synthesis variables: In graft copolymerization reactions, the extent of grafting or efficiency of grafting is a function of synthesis variables. In present study, therefore, the synthesis variables affecting the grafting yields were investigated to achieve the optimum conditions of graft polymerization as discussed below.

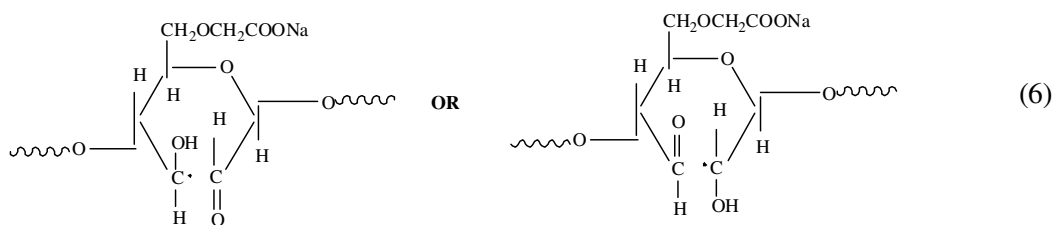
Na-PCMTKP content: The dependency of the amount of Na-PCMTKP ($\overline{DS} = 0.15$) on %G and %GE is well exemplified in Fig. 3a. The continuous decrease in %G with the increase of Na-PCMTKP content becomes noticeable from Fig. 3a. However, the value of %GE increases with the increase in Na-PCMTKP content up to 1.5 g and then decreases with further increment of Na-PCMTKP content. The observed increase in %GE is due to the fact that the number of Na-PCMTKP macro-radicals, available for grafting increase with increase in the amount of Na-PCMTKP up to 1.5 g. However, beyond Na-PCMTKP = 1.5 g, both the values of %G and %GE are found to decrease continuously. These observed trends can be explained by the fact that the viscosity of the reaction medium increase with further increase in the amount of Na-PCMTKP, which hinders the movement of CAN and the monomer, thereby reducing the grafting yields. Similar results have also been reported in the literature [13-15].

Initiator concentration: The influence of CAN concentration on the grafting yields was studied by varying its concentration in the range from $2.5 \times 10^{-3} \text{ mol L}^{-1}$ to $80 \times 10^{-3} \text{ mol L}^{-1}$, keeping all other influential synthesis variables constant (Fig. 3b). As it can be observed that both the values of %G and %GE are increased initially on increasing the initiator concentration up to $30 \times 10^{-3} \text{ mol L}^{-1}$ and then decreased with a further increase

Complex formation



Free radical formation



Graft copolymer formation

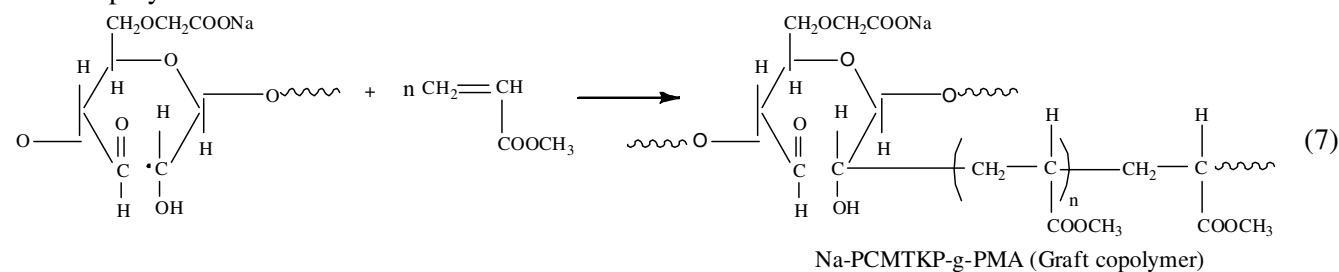


Fig. 2. Mechanism for grafting of MA onto Na-PCMTKP ($\overline{DS} = 0.15$)

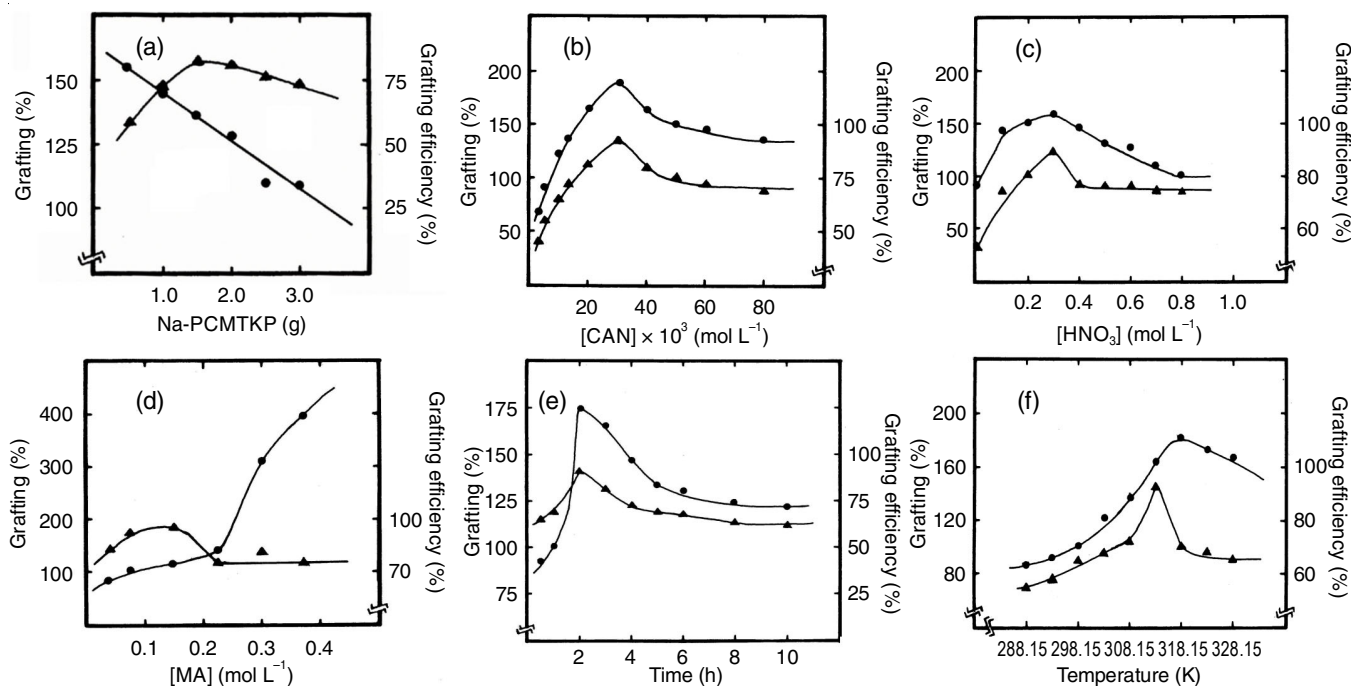


Fig. 3. Influence of (a) amount of sodium salt of partially carboxymethylated tamarind kernel powder (Na-PCMTKP); (b) ceric ammonium nitrate (CAN) concentration; (c) nitric acid (HNO₃) concentration; (d) methyl acrylate (MA) concentration; (e) reaction time and (f) reaction temperature on: —●— %G; or —▲— %GE

in CAN concentration. At the optimum initiator concentration, the best %G and %GE values were achieved to be 187.57% and 92.90%, respectively, where homopolymer (PMA) content was only 7.10%. The observed initial increase in the grafting yields (%G and %GE) could be attributed to the formation of large number of reactive sites on the Na-PCMTKP macromolecules with increasing initiator concentration, which in turn enhances the graft copolymerization. However, beyond [CAN] = 30 × 10⁻³ mol L⁻¹, the excess Ce(IV) starts to take part in the termination of the grafted copolymeric chains as well as the growing homopolymeric chains leading to the lowering of the grafting yields, with the formation of the homopolymer (PMA). Similar initiator concentration dependency of the grafting yields was also reported by other workers [16–18].

Nitric acid (HNO₃) concentration: In order to study the influence of HNO₃ concentration on the grafting yields, the concentration of nitric acid was varied from nil–0.8 mol L⁻¹, keeping fixed the concentrations of CAN (13 × 10⁻³ mol L⁻¹) and MA (0.222 mol L⁻¹), amount of Na-PCMTKP (1.0 dry basis), time (4 h) and temperature (35 °C). Fig. 3c represents the results regarding the effect of HNO₃ concentration on the grafting yields. Both the values of %G and %GE are found to be increased with increase in HNO₃ concentration up to 0.3 mol L⁻¹, at which the highest %G and %GE values obtained were 159.60% and 89.92%, respectively. However, beyond the optimal concentration of the nitric acid (0.3 mol L⁻¹), the values of the grafting yields were found to be decreased.

The results regarding the role of nitric acid in grafting of MA onto Na-PCMTKP (DS = 0.15) may be explained by the fact that ceric ion in water is believed to react as follows [19]:



Thus, ceric ion exists as Ce⁴⁺, [Ce(OH)₃]³⁺ and [Ce-O-Ce]⁶⁺ in an aqueous solution. However, the concentration of these species is found to be dependent on the concentration of nitric acid. Thus, in present case the observed increases in the values of %G and %GE up to [HNO₃] = 0.3 mol L⁻¹ (Fig. 3c) may be attributed to the increase in concentration of Ce⁴⁺ and [Ce(OH)₃]³⁺ and these being smaller in size will form complexes with Na-PCMTKP more effectively than in comparison with [Ce-O-Ce]⁶⁺. With further increase in nitric acid concentration beyond 0.3 mol L⁻¹, these ions which are formed in considerable amount will accelerate the termination of the growing polymeric grafted chains resulting in the decrease in %G and %GE. Similar results are also reported by earlier researchers [16,20,21].

Monomer (MA) concentration: Fig. 3d illustrates the effect of methyl acrylate (MA) concentration on graft copolymerization by changing the concentration of MA from 0.037 to 0.370 mol L⁻¹. It can be noted that %G increases very slowly up to [MA] = 0.222 mol L⁻¹ but subsequently it increases very rapidly. However, the value of %GE increases in the beginning up to [MA] = 0.148 mol L⁻¹ and thereafter it decreases and remains almost constant beyond [MA] = 0.222 mol L⁻¹. The initial increase in the values of %G and %GE with increase in MA concentration could be associated mainly with two reasons *viz.* the greater availability of the monomer (MA) molecules in the proximity of Na-PCMTKP macro-radicals generating more grafting sites and the availability of the extra monomer molecules for grafting. Beyond [MA] = 0.148 mol L⁻¹, the observed decrease in %GE is due to preferential homopolymerization over graft copolymerization. However, beyond [MA] = 0.222 mol L⁻¹, almost constancy in the value of %GE

is observed indicating that formation of homopolymer (as an average of about 23%) takes place at a constant rate.

The observed noticeable increase in %G, beyond $[MA] = 0.222 \text{ mol L}^{-1}$, with further increase in monomer concentration is attributed to the gel effect [22], which not only hinders termination by coupling of the growing polymer chains but also causes swelling of Na-PCMTKP, thereby assisting the diffusion of monomer (MA) to growing grafted chains and active sites on the backbone of Na-PCMTKP, leading to the enhancement in grafting (Fig. 3d). Similar observations have also been reported in the literature [23,24].

Reaction time: The extent of grafting of MA onto Na-PCMTKP ($\overline{DS} = 0.15$) has also been studied at different time intervals from 0.5 to 10 h and the results are shown in Fig. 3e. It can be observed that both the values of the grafting yields (%G and %GE) increase on increasing time period from 0.5 h to 2.0 h. On further increasing time period beyond 2 h, both the values of the grafting yields showed decreasing trend. Thus, the maximum values of %G and %GE were obtained to be 174.28% and 90.16%, respectively at the optimum time, 2h. The observed increase in the grafting yields with increasing time from 0.5 to 2.0 h can be attributed to the occurrence of propagation of grafting chains due to availability of the increasing number of grafting sites on the Na-PCMTKP backbone. However, beyond 2 h, the decrease in the grafting yields is due to the phenomenon of the mutual annihilation of growing grafted chains which may lead to the formation of homopolymer (PMA). Similar results related with polymerization time are also reported in the literature [25,26].

Reaction temperature: The effect of the temperature (Fig. 3f) on the grafting yields was studied in the temperature range between 15° to 55 °C, keeping other synthesis variables fixed. As can be seen from Fig. 3f, the value of %G increases initially up to 45 °C, beyond which it decreases. The observed temperature dependency on %G may be attributed to the fact that with the increase of the temperature from 15° to 45 °C, the rate of diffusion of monomer (MA) and the initiator (CAN) into the Na-PCMTKP backbone increases leading to the increased rate of grafting. However, the observed decrement in the grafting yields could be due to the faster rate of termination and more homopolymerization at higher temperature, as reflected from the grafting efficiency curve (Fig. 3f). Similar

results have been obtained by many workers who have studied the graft copolymerization [27-29].

Thus, from the foregoing discussion, the evaluated optimum reaction conditions of graft copolymerization of MA onto Na-PCMTKP ($\overline{DS} = 0.15$) are: Na-PCMTKP ($\overline{DS} = 0.15$) = 1.5 g (dry basis), $[CAN] = 30 \times 10^{-3} \text{ mol L}^{-1}$; $[HNO_3] = 0.3 \text{ mol L}^{-1}$; $[MA] = 0.148 \text{ mol L}^{-1}$; reaction time = 2 h; reaction temperature = 45 °C and total volume = 150 mL. The maximum values the grafting yields *viz.* %G, %GE and %Hp achieved under the optimal reaction conditions, were 278.27%, 94.38% and 5.62%, respectively.

Overall activation energy of graft copolymerization (E_g): For the estimation of the value of the overall activation energy of graft copolymerization (E_g), the plot of the natural log of % grafting ($\ln \%G$) versus $1/T$ was plotted, for the initial portion of the curve related to the temperature series (*i.e.* 15° to 45 °C) as shown in Fig. 3f [30]. These values fall on a straight line with good correlation coefficient value as it becomes evident from the Arrhenius plot (Fig. 4a), resulting in the estimation of the least square value of the E_g . Therefore, for the present study, E_g was found to be $20.46 \text{ kJ mol}^{-1}$. However, from the earlier results regarding the influence of temperature on the grafting yields obtained in the case of grafting of acrylonitrile onto Na-PCMTKP ($\overline{DS} = 0.15$) [10], the value of E_g was also calculated by following the similar procedure and found to be $10.12 \text{ kJ mol}^{-1}$ (Fig. 4b).

Comparison of reactivity of monomers: The results of the maximum values of the grafting yields (%G, %GE and %Hp), evaluated under optimum reaction conditions and the value of E_g obtained in the present study are tabulated in Table-1 along with those values reported earlier [10] in the case of grafting of acrylonitrile (AN) onto Na-PCMTKP ($\overline{DS} = 0.15$) for the sake of comparison of the reactivity of both these monomers towards grafting. The results of Table-1 confirmed the following reactivity order: AN > MA.

The more reactivity of acrylonitrile (AN) ($\text{CH}_2=\text{CH-CN}$) towards grafting compared to methyl acrylate (MA) ($\text{CH}_2=\text{CH-COOCH}_3$) may be due to the lower electronegativity of nitrogen when compared with oxygen. Thus, as the electronegativity of oxygen is higher, the π -electrons of C=C will be attracted towards oxygen whereas this attraction is less in acrylonitrile. As a result of this, in acrylonitrile, the C=C π -bond is compara-

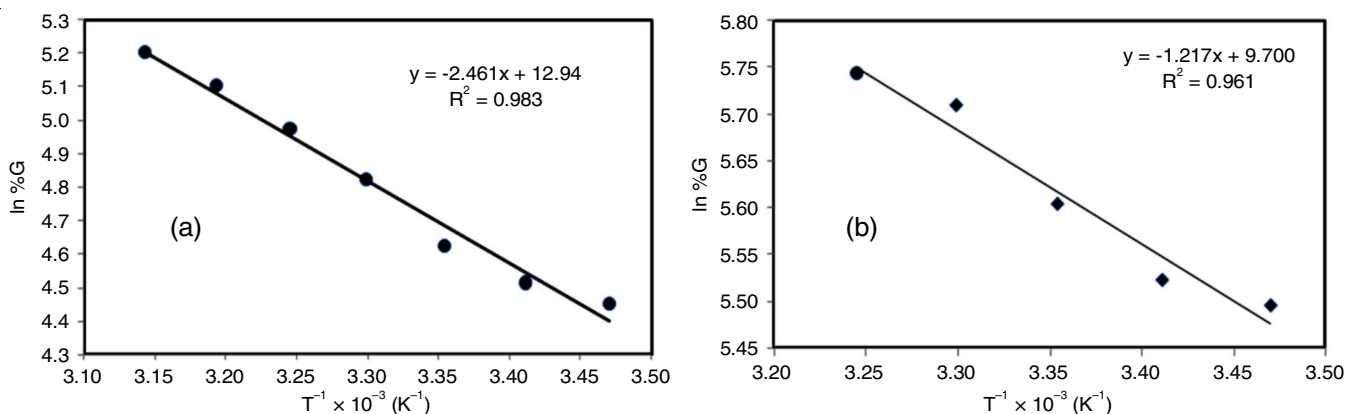


Fig. 4. Plots of $\ln \%G$ versus $1/T$ in the case of grafting of (a) MA and (b) AN onto Na-PCMTKP ($\overline{DS} = 0.15$)

TABLE-1
MAXIMUM VALUES OF GRAFTING YIELDS (UNDER OPTIMUM REACTION CONDITIONS) AS WELL AS THE OVERALL ACTIVATION ENERGY OF GRAFTING (E_g) VALUES OBTAINED IN THE CASE OF GRAFTING OF MA AND AN ONTO Na-PCMTKP ($\overline{DS} = 0.15$)

Sample	Monomer(s)	Grafting yields			E_g (kJ/mol)	Ref.
		G (%)	GE (%)	H_p (%)		
Na-PCMTKP ($\overline{DS} = 0.15$)	MA ^a	278.27	94.38	5.62	20.46	Present study [10]
	AN ^b	413.76	96.48	3.52	10.12	

Optimum reaction conditions for:

MA^a: Na-PCMTKP ($\overline{DS} = 0.15$) = 1.5 g (dry basis); [CAN] = 30×10^{-3} mol L⁻¹; [HNO₃] = 0.30 mol L⁻¹; [MA] = 0.148 mol L⁻¹; Time = 2 h, Temperature = 45 °C and Total volume = 150 mL.

AN^b: Na-PCMTKP ($\overline{DS} = 0.15$) = 1.0 g (dry basis); [CAN] = 20×10^{-3} mol L⁻¹; [HNO₃] = 0.20 mol L⁻¹; [AN] = 0.222 mol L⁻¹; Time = 4 h, Temperature = 40 °C and Total volume = 150 mL.

tively more localized making it inclined to be opened up more easily during graft copolymerization [31].

Secondly, in the case of AN, the observed lower value of E_g (10.12 kJ mol⁻¹) in comparison with MA (20.46 kJ mol⁻¹) indicates the occurrence of grafting reaction with easiness. As a result of this, in the case of AN, the higher values of grafting yields are observed compared to MA (Table-1).

In addition, the values of rate of polymerization (R_p) (eqn. 4) were evaluated at various monomer concentrations as well as at various initiator CAN concentrations in the case of present study of grafting of MA and the results are tabulated in Table-2. Similar values of R_p obtained in the earlier studies of grafting

of AN onto Na-PCMTKP ($\overline{DS} = 0.15$) [10] are also incorporated in Table-2. The comparison of the values of R_p obtained in the case of grafting of MA and AN onto Na-PCMTKP ($\overline{DS} = 0.15$) led to show that the values of the overall rate of polymerization (R_p) in the case of AN are higher compared to MA indicating further that AN is more reactive than MA towards grafting.

Role of reaction medium in grafting: In order to understand the role of reaction medium in the case of grafting of MA onto Na-PCMTKP ($\overline{DS} = 0.15$), the grafting reactions were studied in different water/solvent (%V/V) mixtures, under the evaluated optimum reaction conditions. The solvents used under

TABLE-2
RATE OF POLYMERIZATION (R_p) VALUES IN THE CASE OF THE PRESENT STUDY OF GRAFTING OF MA AS WELL AS AN [10] ONTO Na-PCMTKP ($\overline{DS} = 0.15$) AT VARIOUS INITIATOR (CAN) AND MONOMER (MA) CONCENTRATIONS

[CAN] $\times 10^3$ (mol/L)	$R_p \times 10^5$ (mol L ⁻¹ s ⁻¹)		[Monomer] (mol/L)	$R_p \times 10^5$ (mol L ⁻¹ s ⁻¹)	
	MA ^a	AN ^a		MA ^b	AN ^b
2.5	0.84	1.78	0.037	0.54	1.35
5.0	0.92	1.93	0.074	0.59	1.88
10.0	1.01	2.42	0.148	0.67	2.44
13.0	1.02	2.85	0.222	1.04	2.85
20.0	1.06	3.17	0.296	2.08	3.69
30.0	1.09	3.14	0.370	2.85	4.17
40.0	1.08	3.14			
50.0	1.07	3.12			
60.0	1.11	3.12			
80.0	1.09	3.12			

^aReaction conditions in the case of MA and AN: Na-PCMTKP = 1.0 g (dry basis); [CAN] = varied as shown; [HNO₃] = 0.10 mol L⁻¹; [Monomer] = 0.222 mol L⁻¹; Time = 4 h; Temperature = 35 °C and Total volume = 150 mL.

^bReaction conditions in the case of MA and AN: Na-PCMTKP = 1.0 g (dry basis); [CAN] = 13×10^{-3} mol L⁻¹; [HNO₃] = 0.10 mol L⁻¹; [Monomer] = varied as shown; Time = 4 h; Temperature = 35 °C and Total volume = 150 mL; MA = Methyl acrylate; AN = Acrylonitrile.

TABLE-3
INFLUENCE OF REACTION MEDIUM ON GRAFTING OF METHYL ACRYLATE (MA) ONTO SODIUM SALT OF PARTIALLY CARBOXYMETHYLATED TAMARIND KERNEL POWDER (Na-PCMTKP, $\overline{DS} = 0.15$)^a

Water/solvent ratio (v/v)	Methanol		Ethanol		<i>n</i> -Propanol		<i>n</i> -Butanol	
	Grafting (%)	Grafting efficiency (%)	Grafting (%)	Grafting efficiency (%)	Grafting (%)	Grafting efficiency (%)	Grafting (%)	Grafting efficiency (%)
100:00	278.27	94.38	278.27	94.38	278.27	94.38	278.27	94.38
75:25	200.08	90.14	194.21	90.00	192.68	90.80	192.52	91.18
50:50	168.91	85.80	143.91	84.19	140.83	81.33	139.94	80.71
25:75	100.18	78.13	98.47	76.08	98.09	75.47	97.30	76.38
00:100	89.74	73.51	80.69	70.38	79.55	71.29	79.04	68.50

^aReaction conditions: Na-PCMTKP ($\overline{DS} = 0.15$) = 1.5 g (dry basis), [CAN] = 30×10^{-3} mol L⁻¹; [HNO₃] = 0.30 mol L⁻¹; [MA] = 0.148 mol L⁻¹; Time = 2 h; Temperature = 45 °C and Total volume = 150 mL.

study were methanol, ethanol, *n*-propanol and *n*-butanol. From Table-3, it can be observed that in the case of all the solvents studied, the value of %G decreases with increasing the solvent ratio in the water/solvent mixtures. Secondly, for all different values of water/solvent ratios, the value of %G decreases from methanol to *n*-butanol. Among all the solvents studied with different values of water/solvent ratios, the most advantageous medium for grafting to occur with higher value of the percentage grafting (%G = 200.08) is the water/methanol mixture having the proportion of 75:25. Thus, the observed differences in %G obtained with water/solvent mixtures (as graft copolymerization medium) could be explained on the basis of the differences in (i) ability to swell trunk polymer; (ii) miscibility with monomer (MA); (iii) extent of access and diffusion of monomer to the grafting sites on the Na-PCMTKP and (iv) termination *via* chain transfer reaction. The first three factors will favour the increase in grafting but the last factor will adversely affect the grafting. The results (Table-3), therefore, show that the reaction medium plays an important role in graft copolymerization reaction. Lenka [32] also observed similar trend for the alcohols *i.e.* methanol > ethanol > propanol > butanol in the case of grafting of methyl methacrylate on nylon-6.

Characterization of graft copolymerization

FTIR Studies: Fig. 5a shows the IR spectrum of Na-PCMTKP, from which a strong and broad absorption band at $\sim 3433\text{ cm}^{-1}$ is attributed to the -OH stretching. The absorption band at $\sim 2424\text{ cm}^{-1}$ is assigned to the -CH stretching. The asym-

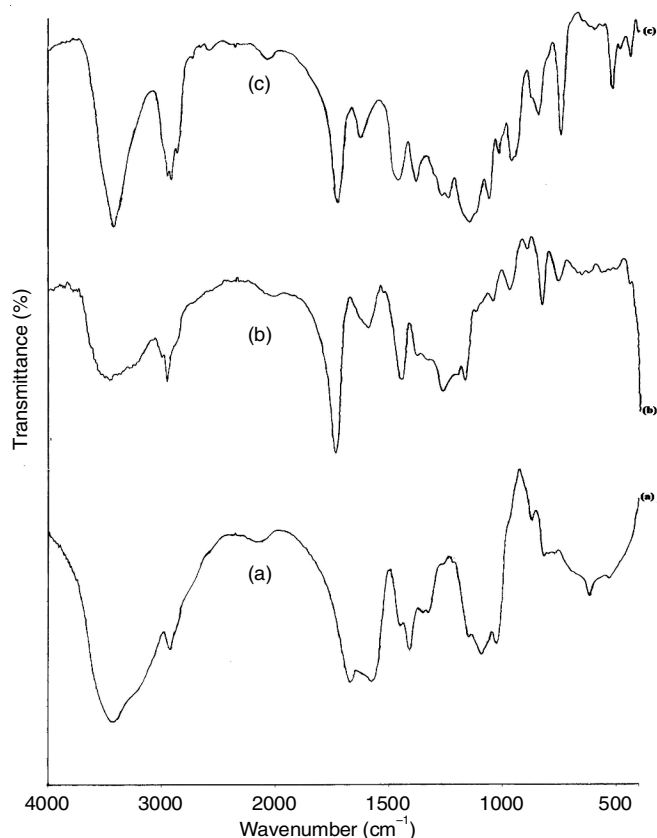


Fig. 5. FT-IR spectra of (a) Na-PCMTKP ($\overline{DS} = 0.15$); (b) Na-PCMTKP-g-PMA (%G=278.27) and (c) PMA

metric and symmetric vibrations of -COO- moiety are assigned to ~ 1641 and $\sim 1423\text{ cm}^{-1}$, respectively providing the proof for the incorporation of carboxymethyl groups in tamarind kernel powder.

The IR spectrum of the graft copolymer, Na-PCMTKP-g-PMA (%G = 278.27) (Fig. 5b) showed an additional strong absorption band at $\sim 1750\text{-}1730\text{ cm}^{-1}$ assigned to C=O stretching of ester group (-COOCH₃) characteristic of methacrylates. Fig. 5c represents the IR spectrum of PMA sample (isolated by the hydrolysis method) wherein the presence of -C=O stretching band appeared at about $1750\text{-}1730\text{ cm}^{-1}$ is attributed to the fact that hydrolysis of the graft copolymer, Na-PCMTKP-g-PMA sample gives back the grafted chains (PMA).

Thus, the results of Fig. 5a-c provide a significant evidence of grafting of MA onto Na-PCMTKP ($\overline{DS} = 0.15$).

Thermal studies: Thermogravimetric curves obtained at a scan rate of $10\text{ }^{\circ}\text{C}/\text{min}$ for Na-PCMTKP ($\overline{DS} = 0.15$), Na-PCMTKP-g-PMA (%G = 278.27) and PMA samples in nitrogen atmosphere are depicted in Fig. 6. It can be seen that Na-PCMTKP sample shows two steps of degradation. The sample begins to decompose at about $220\text{ }^{\circ}\text{C}$ and loses its weight very slowly up to $400\text{ }^{\circ}\text{C}$ involving about 57% weight loss. The second decomposition step is immediately followed and marked with a rapid weight loss in the temperature range $400\text{-}590\text{ }^{\circ}\text{C}$ during which the sample loses 38% of its weight. The maximum rates of weight loss for the first and second decomposition steps are observed at $300\text{ }^{\circ}\text{C}$ and $495\text{ }^{\circ}\text{C}$, respectively. The degradation is observed to be completed at about $590\text{ }^{\circ}\text{C}$ leaving about 5% residual weight.

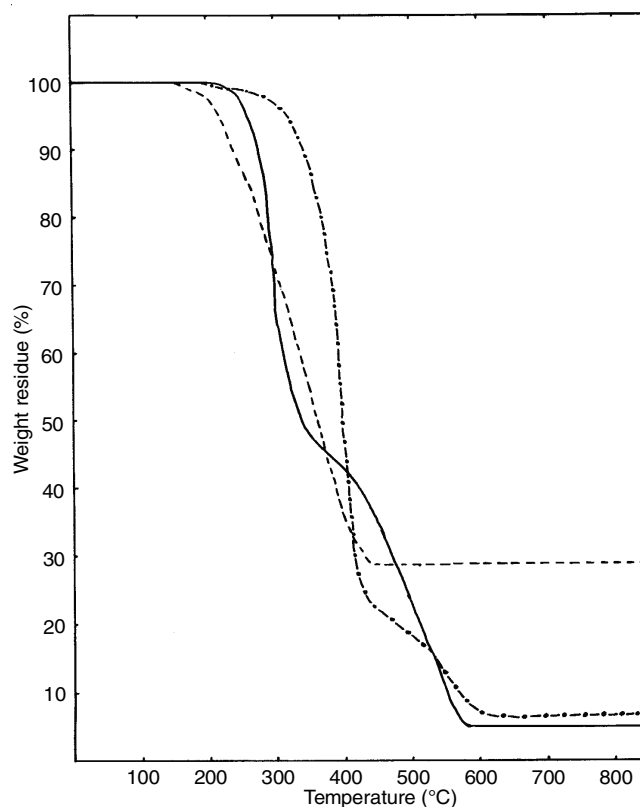


Fig. 6. TG thermograms for (—) Na-PCMTKP ($\overline{DS} = 0.15$); (---) Na-PCMTKP-g-PMA (%G=278.27) and (-●-) PMA at $10\text{ }^{\circ}\text{C}/\text{min}$

However, the graft copolymer (Na-PCMTKP-*g*-PMA, %G = 278.27) sample shows a single step of degradation. The decomposition starts at 160 °C and proceeds at a slower rate up to 270 °C, involving about 16% weight loss. There exists 53% weight loss in temperature range 270-430 °C. The maximum rate of weight loss occurs at 330 °C. The overall degradation leaves about 28% residue. In case of PMA, the overall degradation involves two steps, the first step encompassing a temperature range 210 to 450 °C, involves about 77.5% weight loss, the rate of weight loss reaching a maximum at 395 °C. This step is immediately followed by the second step involving about 16% weight loss over a temperature range 450-630 °C with a maximum rate of weight loss at 540 °C. The homopolymer sample leaves about 6.5% residue.

Thermogravimetric analysis data derived from the primary thermograms of Na-PCMTKP ($\overline{DS} = 0.15$), Na-PCMTKP-*g*-PMA (%G = 278.27) and PMA are tabulated in Table-4. It can be revealed upon examining the IPDT values of the samples that the overall thermal stability of Na-PCMTKP ($\overline{DS} = 0.15$) has been decreased upon grafting of MA onto it. The observed decrease in the thermal stability of the graft copolymer is expected since polyacrylates are known to depolymerize upon pyrolysis [29]. However, the thermal stability of PMA is found to be higher compared to Na-PCMTKP ($\overline{DS} = 0.15$) and the graft copolymer.

Scanning electron microscopy (SEM) studies: Scanning electron micrographs of ungrafted and MA grafted Na-PCMTKP (with %G = 278.27) are shown in Figs. 7a and b, respectively.

The surface morphology of Na-PCMTKP ($\overline{DS} = 0.15$) shows the clustered granular structure (Fig. 7a), which may be attributed to its branched structure and interactions of the carboxylic groups present on it. The grafting of MA onto Na-PCMTKP ($\overline{DS} = 0.15$) has drastically changed the topology of Na-PCMTKP sample, in terms of lumpy morphology (Fig. 7b) providing further an additional evidence of grafting.

Conclusion

In this study, the optimum reaction conditions have been established first time in case of free radical graft copolymerization of methyl acrylate onto Na-PCMTKP ($\overline{DS} = 0.15$) using initiator pair of CAN/HNO₃ as redox system. At optimum conditions, the maximum values of the grafting yields achieved are %G = 278.27, %GE = 94.38 and %Hp = 5.62. The influence of various synthesis variables on the grafting yields has also been studied. From the results of temperature dependency on grafting, the overall activation energy of graft copolymerization (E_g) was found to be 20.46 kJ mol⁻¹. The reactivity of methyl acrylate (MA) has been compared with that of acrylonitrile (AN, from the earlier studies) in terms of their structures, the E_g and the R_p (overall rate of polymerization) values at various monomers (MA and AN) and initiator (CAN) concentrations. The plausible explanation for the observed order of reactivity (AN > MA) towards graft copolymerization has also been provided. The role of reaction medium in the graft copolymerization has also been studied and it was observed that the magnitude of grafting differs notably with the type and ratio

TABLE-4
THERMAL ANALYSIS DATA OF Na-PCMTKP ($\overline{DS} = 0.15$), Na-PCMTKP-*g*-PMA (%G = 278.27) AND PMA SAMPLES

Sample	T_i °C (IDT)	T_f °C (FDT)	T_{max} (°C)		T_{10} (°C)	T_{50} (°C)	IPDT* (°C)
			Step 1	Step 2			
Na-PCMTKP	220	590	300	495	275	340	393.90
Na-PCMTKP- <i>g</i> -PMA	160	425	325	–	245	365	305.75
PMA	210	630	395	540	350	400	424.20

IPDT = $A^(T_f - T_i) + T_i$, where A^* is the fractional area under the Thermogravimetric curve normalized with respect to residual weight, T_f and T_i are temperatures of completion of weight loss and initiation of weight loss respectively.

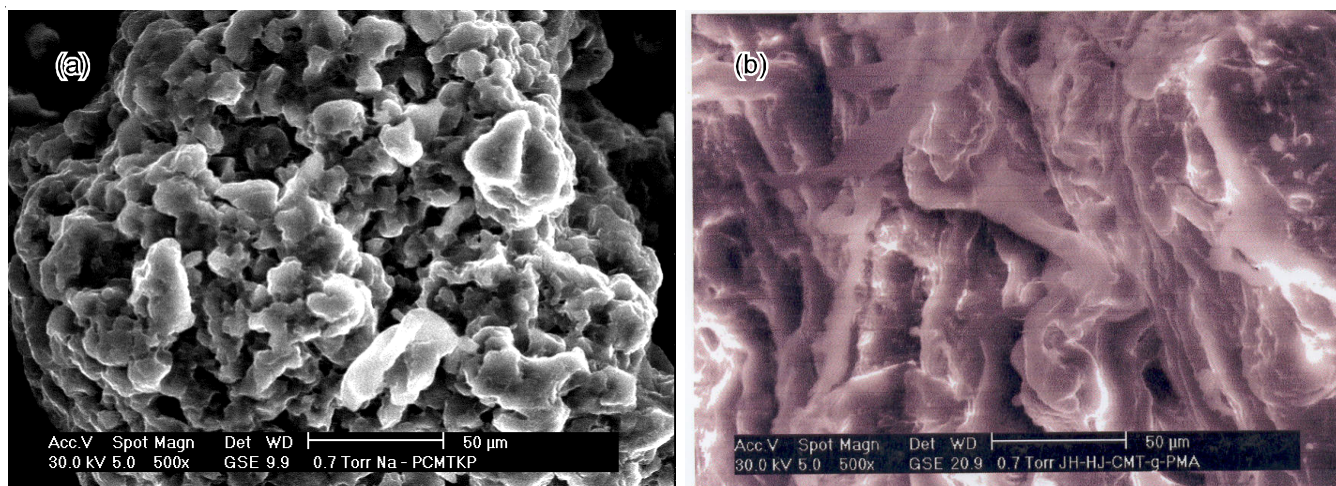


Fig. 7. Scanning electron micrographs of (a) sodium salt of partially carboxymethylated tamarind kernel powder (Na-PCMTKP, $\overline{DS} = 0.15$) (500X) and (b) Na-PCMTKP-*g*-PMA (%G = 278.27) (500X)

of solvent used in the mixture. The %G values have been found to be higher for the case of water-methanol system than for the water-ethanol, water-propanol and water-butanol systems. FTIR, TGA and SEM techniques have been used successfully for providing the evidence of grafting. The synthesized graft copolymer, Na-PCMTKP-g-PMA, after treating with hydroxylamine in the alkaline medium may find its potential application as a novel metal adsorbent.

CONFLICT OF INTEREST

The authors declare that there is no conflict of interests regarding the publication of this article.

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