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MW-assisted synthesis of carboxymethyl tamarind kernel polysaccharide-*g*-polyacrylonitrile: Optimization and characterization

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ABSTRACT

Microwave-assisted synthesis of graft copolymer of carboxymethyl tamarind seed polysaccharide and polyacrylonitrile was carried out. The effect of formulation and process variables on grafting efficiency of carboxymethyl tamarind kernel polysaccharide-*g*-poly(acrylonitrile) was studied using response surface methodology. The results revealed that the significant factors affecting grafting efficiency were concentrations of ammonium persulphate, acrylonitrile and interaction effects of ammonium persulphate and acrylonitrile concentrations. The optimal calculated parameters were found to be microwave exposure time—99.48 s, microwave exposure power—160 W, concentration of acrylonitrile—0.10% (w/v), concentration of ammonium persulphate—40 mmol/l, which provided graft copolymer with grafting efficiency of 96%. The formation of graft copolymer was confirmed by FT-IR studies and validated by scanning electron micrographs. Thermogravimetric analysis indicated higher thermal stability of graft copolymer and X-ray diffraction study revealed increase in crystallinity on graft polymerization. Further, the graft copolymer showed pH dependant swelling.

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1. Introduction

Polysaccharides are found abundantly in nature ranging from plant, animal and marine sources. Further due to their non-carcinogenicity, biocompatibility and easy availability, they serve as renewable reservoirs for synthesis of multifunctional materials (BeMiller & Whistler, 1992). Among the various modification approaches grafting is one of the most promising. In grafting monomer is covalently bonded on to the polymer backbone. It provides means of synthesizing hybrid polymers, having the advantages of two or more component polymers. A number of techniques such as chemical, radiation, photochemical, plasma induced and enzymatic grafting have been employed (Bhattacharya & Misra, 2004). Conventional grafting procedures are characterized by polysaccharide backbone degradation and formation of undesired homopolymer *via* concurrent competing reactions which lower the percentage grafting. These problems can be overcome by use of microwave assisted reactions, which provide graft copolymer with higher percentage grafting in a shorter duration of time. Moreover microwave assisted reactions can be carried out in a open reaction vessel with reduced solvent content unlike the conventional reactions which require inert atmosphere (Singh, Kumar, & Sanghi, 2012).

A number of vinyl monomers such as acrylamide (Singh, Tiwari, Tripathi, & Sanghi, 2004), acrylic acid, acrylonitrile, methyl acrylate etc. have been grafted on polysaccharides such as gum acacia, chitosan (Liu, Wang, & Wang, 2007), and tamarind seed polysaccharide (Ahuja, Kumar, & Kumar, 2013). Microwave assisted graft copolymer reactions are influenced by number of factors such as microwave exposure time, microwave exposure power (Kumar, Singh, & Ahuja, 2009), concentration of vinyl monomer, concentration of polysaccharide backbone, concentration of initiator etc.

During earlier study acrylonitrile grafted psyllium (Mishra, Srinivasan, & Gupta, 2003), okra (Mishra, & Pal, 2007), chitosan (Shankar, Gomathi, Vijyalakshmi, & Sudha, 2014) have been employed as flocculant and superabsorbing polymers. In the present study microwave assisted graft copolymerization of acrylonitrile on carboxymethyl tamarind kernel polysaccharide has been optimized using central composite experimental design. The optimized batch of graft copolymer was further characterized by FT-IR, X-ray diffraction, thermogravimetric analysis, scanning electron microscopy and swelling characteristics.

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2. Experimental

2.1. Materials

Carboxymethyl tamarind kernel polysaccharide (CMTKP) was procured from Hindustan Gums and Chemicals Pvt. Ltd. (Bhiwani, India). Acrylonitrile (AN) was obtained from S.D. Fine Chem Ltd. (Mumbai, India). Ammonium persulphate (APS) GR (99% pure) was procured from Sisco Research Laboratory (Mumbai, India). All other chemicals of reagent grade were used as such.

2.2. Synthesis of CMTKP-g-poly(acrylonitrile)

Microwave-assisted grafting of AN on CMTKP was done using previously reported method (Malik & Ahuja, 2011). Briefly, powdered CMTKP (1% w/v) was added to aqueous solution of acrylonitrile (0.1–0.4%, w/v) and mixed thoroughly in a reaction vessel. Desired amount of APS (10–40 mmol/l) was added to the above solution and the reaction vessel was placed on turntable of a domestic microwave oven (2300 ET-B, Bajaj Electricals Ltd., Mumbai, India). Microwave irradiation at power of 160–480 W, for time of 60–120 s was carried out. After required exposure to microwave irradiation, reaction mixture was cooled by placing it in cold water. The resultant graft copolymer was then precipitated with methanol and unreacted residues were removed by washing with methanol (80%). Precipitated graft copolymer was dried in hot air oven at 60 °C and pulverized. Grafting efficiency was calculated using the following formula.

$$\%GE = \frac{W_1 - W_0}{W_2} \times 100 \quad (1)$$

$\%GE$ is grafting efficiency, W_1 is weight of graft copolymer, W_0 is weight of polysaccharide and W_2 is weight of monomer.

2.3. Experimental design

Synthesis of CMTKP-g-PAN was optimized using 3-level, 4-factor central composite experimental design. Concentrations of AN (A), APS (X_2), microwave irradiation time (X_3) and microwave power (X_4) were used as independent variables on the basis of preliminary trials. Grafting efficiency was selected as dependent variable and the effect of independent variables on grafting efficiency was studied at 3 levels i.e., low (−1), middle (0), high (+1). The experimental design and statistical analysis of data were done using the Design Expert software (version 7.0.0 Stat-Ease-Inc. Minneapolis MN).

2.4. Characterization

2.4.1. FTIR spectra

IR spectra of CMTKP and CMTKP-g-PAN samples were taken in KBr pellets using Fourier transform infrared spectrophotometer (Perkin Elmer, USA) between 400 and 4000 cm^{-1}.

2.4.2. Thermogravimetric analysis

Thermal behaviour of CMTKP and CMTKP-g-PAN was recorded under constant nitrogen purge of 100 ml/min in a temperature range of 25–600 °C at heating rate of 10 °C/min with the help of simultaneous thermal analyzer (SDT,Q-600, TA Instruments, USA).

2.4.3. X-ray diffraction

Powder diffraction spectra of CMTKP and CMTKP-g-PAN samples were recorded employing X-ray diffractometer (Miniflex II, Rigaku Japan) copper Kα-radiation generated at 40 kV and 35 mA in the differential angle range of 0–80° (2θ).

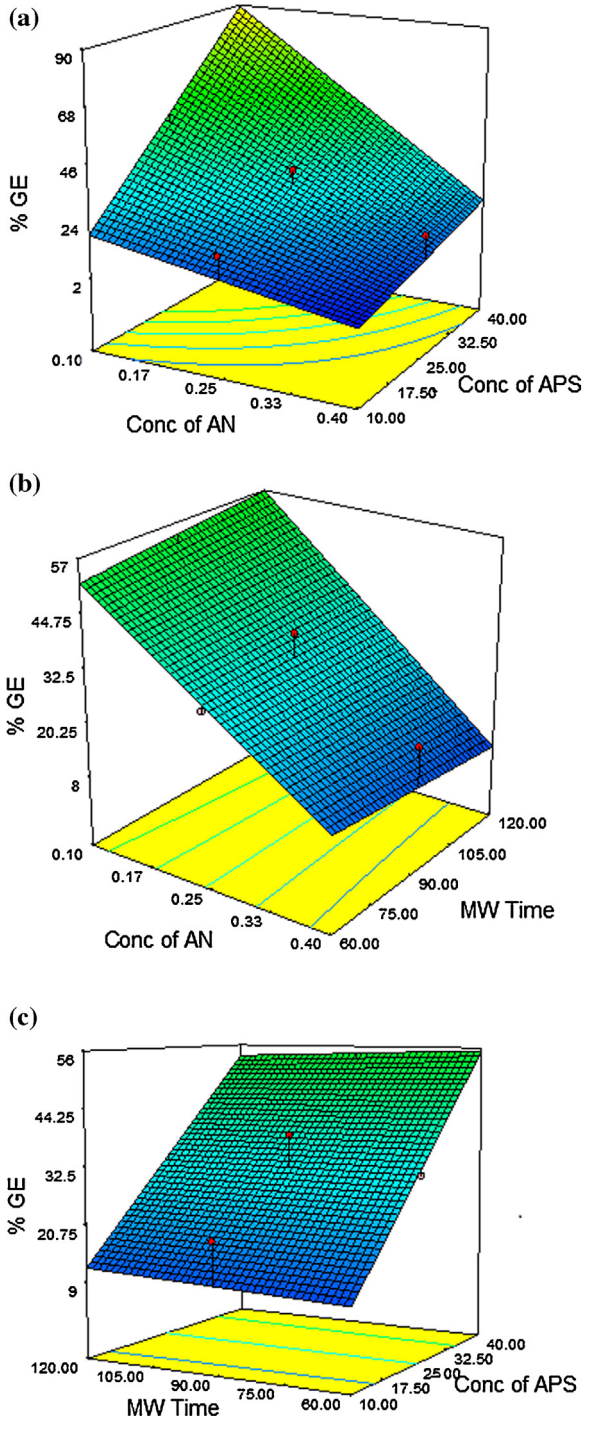

Fig. 1. Response surface plots showing the combined effect of (a) concentrations of acrylonitrile and ammonium persulphate, (b) concentration of acrylonitrile and MW exposure time and (c) concentration of ammonium persulphate and MW exposure time.

2.4.4. Scanning electron microscopy

Scanning electron micrographs of CMTKP and CMTKP-g-PAN powder samples were recorded using SEM (JEOL, JSM-6100). The photomicrographs were taken at accelerating voltage of 15 kV.

2.4.5. Swelling behaviour

Swelling behaviour of optimized batch of CMTKP-g-PAN was studied at pH 2.0, 6.6 and 8.0. An accurately weighed sample of optimized batch of graft copolymer was placed in basket of

Table 1
Effect of various factors on grafting efficiency of various batches prepared using central composite experimental design.

Batch no.	Conc. of AN X_1 (%w/v)	Conc. of APS X_2 (mmol/l)	Time X_3 (s)	Power X_4 (W)	*GE* (%)
1	0.1	10	60	160	21.0
2	0.4	10	60	160	5.0
3	0.1	40	60	160	94.0
4	0.4	40	60	160	23.5
5	0.1	10	120	160	34.0
6	0.4	10	120	160	5.75
7	0.1	40	120	160	83.0
8	0.4	40	120	160	19.5
9	0.1	10	60	480	22.0
10	0.4	10	60	480	1.25
11	0.1	40	60	480	90.0
12	0.4	40	60	480	35.0
13	0.1	10	120	480	15.0
14	0.4	10	120	480	4.0
15	0.1	40	120	480	117.0
16	0.4	40	120	320	16.25
17	0.1	25	90	320	43.0
18	0.4	25	90	320	20.25
19	0.25	25	90	320	19.6
20	0.25	25	90	320	40.8
21	0.25	25	60	320	31.2
22	0.25	25	120	320	29.6
23	0.25	25	90	160	43.2
24	0.25	25	90	480	15.2
25	0.25	25	90	320	16.4
26	0.25	25	90	320	26.0
27	0.25	25	90	320	18.8
28	0.25	25	90	320	24.0
29	0.25	25	90	320	38.0
30	0.25	25	90	320	29.6

dissolution apparatus and immersed in buffer media of pH 2.0 (HCl buffer), 6.6 and 8.0 (phosphate buffer). At various time intervals, baskets were taken out of swelling media and weighed immediately after blot drying with blotting paper (Malik, Kumar & Ahuja 2012).

3. Results and discussion

3.1. Synthesis of CMTKP-g-PAN

Graft modification of carboxymethyl tamarind kernel polysaccharide was achieved employing acrylonitrile as a vinyl monomer using microwave-assisted reactions. Polysaccharide molecules being large in size cannot migrate under the influence of rapidly changing electric field component of microwaves but its pendent hydroxyl groups show localized rotation contributing to the dielectric heating, which results in enhancement of reaction rates specifically at these groups (Singh et al., 2012). In addition MW radiations are reported to lower the Gibbs energy of activation of reactions enhancing the reaction rates (Singh, Tripathi, Tiwari, & Sanghi, 2005).

Further ammonium persulphate used as free radical initiator provides the free radicals which also abstract hydrogen atom from CMTKP molecule yielding CMTKP macroradicals. These macroradicals initiate the chain reaction and further propagate the reaction by reacting with acrylonitrile monomer providing acrylonitrile free radicals which results in a series of free radical chain reactions yielding CMTKP-*g*-PAN and polyacrylonitrile homopolymer which can be elucidated by the following scheme.

Chain initiation

$$S_2O_8^{2-} \rightarrow 2SO_4^{*-}$$

$$CMTKPOH + R^* \rightarrow CMTKPO^* + RH$$

$$R^* + M \rightarrow RM^*$$

where R^* is SO_4^{*-} and CMTKPOH is carboxymethyl tamarind kernel polysaccharide, and M is acrylonitrile.

Propagation

$$CMTKPO* + M?CMTKPOM*$$

$$CMTKPOM^* + M \rightarrow CMTKPOM_1^*$$

$$CMTKPOM^* + M \rightarrow CMTKPOM_2^*$$

$$CMTKPOM_{n-1}^* + M \rightarrow CMTKPOM_n^*$$

$$RM^* + M \rightarrow RM_1^*$$

$$RM^* + M \rightarrow RM_2^*$$

$$RM_{m-1}^* + M \rightarrow RM_m^*$$

Termination

$$CMTKPOM_n^* + CMTKPOM_m^* \rightarrow \text{Graft copolymer}$$

$$CMTKPOM_n^* + RM_m^* \rightarrow \text{Graft copolymer}$$

$$RM_n^* + RM_m^* \rightarrow \text{Homopolymer}$$

3.2. Effect of processing and formulation variables on synthesis of CMTKP-g-PAN

Table 1 details the results of various batches of graft copolymerization carried out using the experimental design. It was observed that the response (*GE*) fitted best into the response surface two-factorial model (2FI) with backward elimination. The mathematical

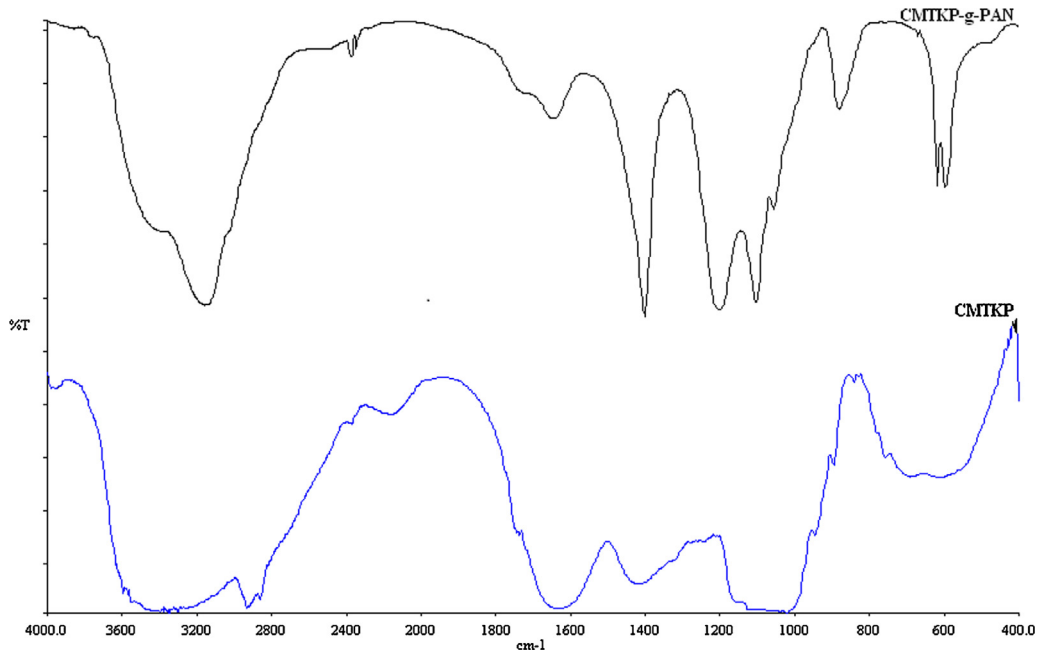

Fig. 2. FT-IR spectra of CMTKP and CMTKP-*g*-PAN.

relationship between the independent variables and %*GE* can be expressed by the following equation:

$$Y(\%GE) = +32.73 - 21.58 \times X_1 + 21.75 \times X_2 + 0.064 \times X_3 - 13.36 \times X_1 \times X_2 - 2.58 \times X_1 \times X_3 - 1.02 \times X_2 \times X_3 \quad (2)$$

The results revealed that concentrations of AN (X_1) exerted a significant antagonistic influence on grafting efficiency while concentrations of APS (X_2) showed a significant synergistic effect on grafting efficiency. However, there was no significant effect of microwave time (X_3) on grafting efficiency. Further the

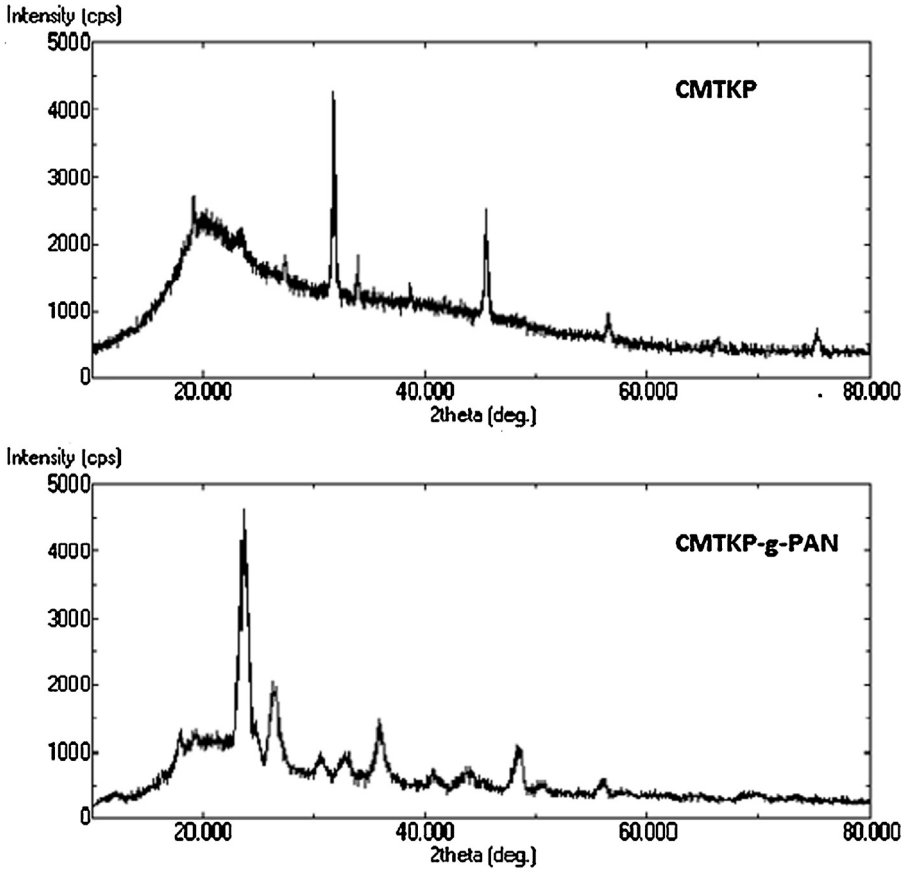

Fig. 3. X-ray diffraction of CMTKP and CMTKP-*g*-PAN.

interaction effect of concentrations of AN and APS affected the response antagonistically. Significance of model was estimated by applying ANOVA analysis which showed the model to be significant ($P < 0001$) with non significant 'lack-of-fit'. Further higher values of R^2 (0.8784) and reasonably good agreement between the values of 'predicted R^2' (0.7802) and 'adjusted R^2' (0.8466) indicate the design model to be reliable. The value of adequate precision (16.992), which should be greater than four indicate adequate signal and suitability of model to navigate the design.

Fig. 1(a–c) exhibits the combined effect of different independent variables on grafting efficiency of CMTKP-*g*-PAN. Fig. 1(a) shows the combined effect of concentrations of AN and APS on *%GE*. It can be inferred from the plot that increasing the concentration of APS at lowers levels of AN results in increase in grafting efficiency. On the other hand the effect of increasing concentration of APS at higher values of AN is less pronounced. Increasing the concentration of AN results in decrease in grafting efficiency. These results can be explained by the fact that increasing AN concentration results in formation of more amount of homopolymer which decreases grafting efficiency. At lower levels of AN increasing APS concentration results in formation of more AN macroradicals, which react with sufficient amount of CMTKP backbone to yield graft copolymer. However, increasing the AN concentration results in formation of excess amount of AN macroradicals, which due to insufficient polysaccharide backbone react themselves to give homopolymer thereby decreasing the grafting efficiency.

Fig. 1(b) shows the combined effect of concentration of AN and microwave exposure time on *GE*. The effect of concentration of AN on grafting efficiency is more pronounced than the effect of MW exposure duration. Increasing the concentration of AN results in decrease in grafting efficiency which may be attributed to formation of greater amount of homopolymer. The lower concentration of acrylonitrile and exposure for higher duration favours the formation of graft copolymer with higher percentage grafting.

It can be observed from Fig. 1(c) that concentration of APS has more pronounced effect on grafting efficiency than microwave exposure time. Increasing concentration of APS resulted in increase in efficiency of grafting reaction. APS is a free radical initiator, increasing its concentration results in formation of greater amount of free radicals which result in increase in formation of graft copolymer. Further, it can be inferred from the results that MW exposure time of 60 s is sufficient and increasing the exposure time has no effect on *GE* at any given concentration of APS.

A numerical optimization tool of Design Expert software using the desirability approach was used to synthesize graft copolymer of desired % grafting efficiency. The optimal parameters were calculated with the goal of optimization of maximizing the % grafting efficiency setting the constraints for concentrations of AN (X_1) and APS (X_2), and MW exposure time (X_3) within the range and MW irradiation power (X_4) set at 160 W. The optimization tool provided us with 24 different sets of solutions. An optimal batch with concentrations of AN (X_1)—0.10% (w/v), APS (X_2)—40 (mmol/l), MW exposure time (X_3)—99.48 s and MW irradiation power (X_4)—160 W provided a graft copolymer with grafting efficiency of 96% (predicted 89.14%).

3.3. Characterization of Graft copolymer

The optimized batch of graft copolymer was further characterized by FT-IR, Thermogravimetric, X-ray diffraction and SEM analysis. Fig. 2 depicts the FT-IR spectra of CMTKP and CMTKP-*g*-PAN. The spectra of CMTKP shows a broad band at 3165.58 cm^{-1} which is due to OH stretching, while C—O stretching is confirmed by sharp peak at 1400.41 cm^{-1}. Peaks at 1219.26 cm^{-1} and 1101.32 cm^{-1} can be attributed to C—O—C stretch of ether. The spectra of CMTKP-*g*-PAN

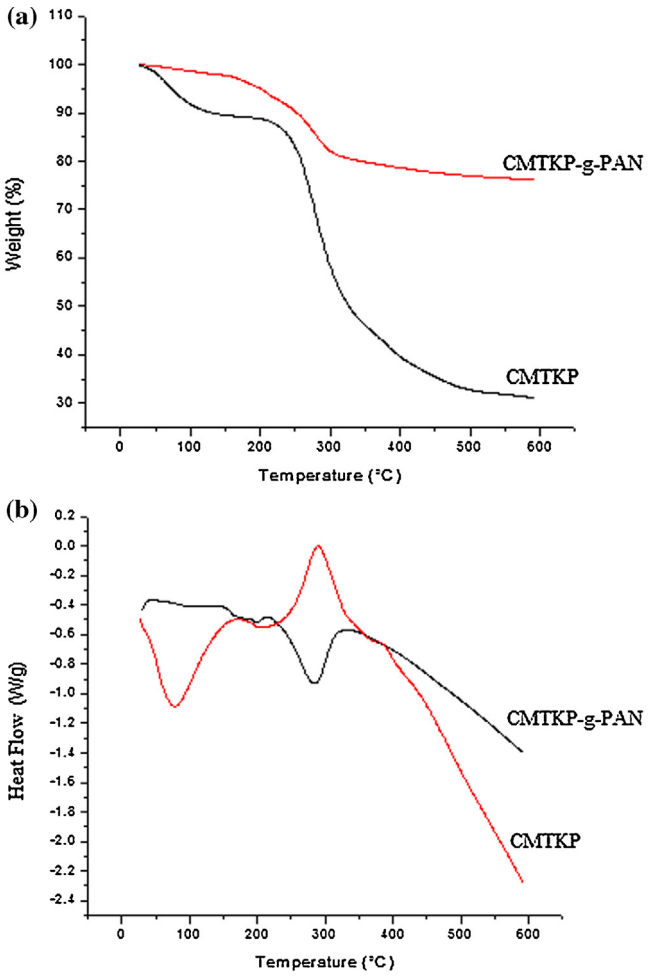

Fig. 4. (a) TGA and (b) DSC curves of CMTKP and CMTKP-g-PAN.

exhibited the broad band at 3416.20 cm^{-1} while the peak appearing at 2926.16 cm^{-1} is due to symmetric stretching of methylene group. Peak at 1638.91 cm^{-1} confirms the presence of C=C of monomer. Grafting of acrylonitrile is confirmed by the presence of peak at 2156.86 cm^{-1} which is due to nitrile stretching.

Fig. 3 shows the powder X-ray diffraction spectra of CMTKP and CMTKP-*g*-PAN. The diffraction pattern of CMTKP shows the characteristic peaks at 31.84°, 33.96°, 45.56° and 75.38° (2θ). On the other hand diffractogram of CMTKP-*g*-PAN displays the characteristic sharp peaks at 23.72°, 26.44°, 31.30°, 32.86°, 35.92°, 48.28° (2θ). The presence of large number of sharp peaks with greater intensity, indicate increase in degree of crystallinity on graft modification.

It can be observed from Fig. 4(a) that CMTKP-g-PAN is thermally more stable than CMTKP. On heating CMTKP from 25 to 110 °C it losses only 10% of weight and then degrades slowly from 110 to 236 °C with 5% of weight loss. Then it starts degrading at somewhat slower rate losing 25% of weight at 296–396 °C and finally attains a weight loss of 68% at decomposition temperature of 501 °C. TGA curve of CMTKP-*g*-PAN shows a single stage of decomposition on heating it from 25 °C till 100 °C it losses only 1.4% of weight. On further heating till 185 °C it losses 2% more weight and then it starts degrading at a faster rate losing up to 20% of its original weight at temperature of 343 °C.

Fig. 4(b) displays the DSC thermograms of CMTKP and CMTKP-*g*-PAN. The thermogram of CMTKP shows a sharp peak at 78 °C followed by an exothermic peak at 290 °C. Thermogram of CMTKP-*g*-PAN shows a broad endothermic peak at 284 °C. Thus shifting

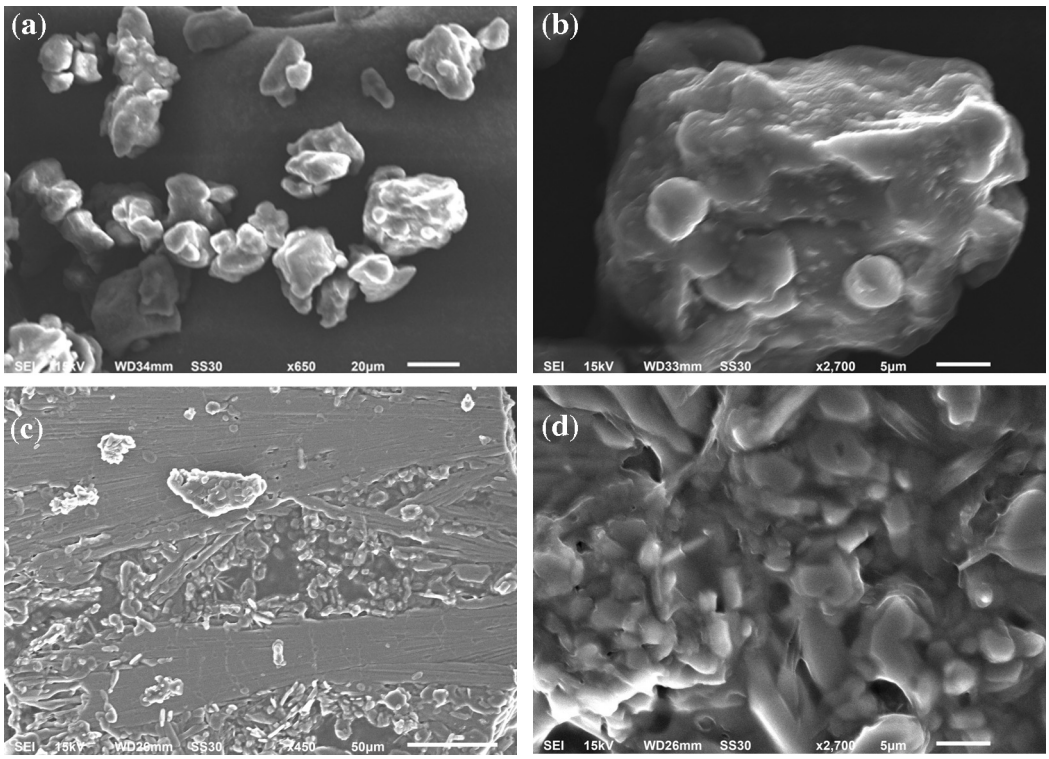

Fig. 5. Scanning electron micrograph showing (a) shape and (b) surface of CMTKP, (c) shape and (d) surface of CMTKP-*g*-PAN.

Table 2
Swelling behaviour of optimized batch of graft co-polymer.

	pH 2.0	pH 6.6	pH 8.0
%	126.6	104.2	171.4
Swelling	125.1	102.8	172.9
Mean ± SD	127.3	103.4	171.1
	126.27 ± 1.04	103.46 ± 0.70	171.8 ± 0.96

of endothermic peak and disappearance of an exotherm indicate modification of CMTKP has taken place. The shifting of endotherm to higher temperature also indicates the increase thermal stability of graft copolymer over native gum.

Fig. 5(a) and (b) presents shape and surface morphology of CMTKP while Fig. 5(c) and (d) shows shape and surface morphology of CMTKP-*g*-PAN. CMTKP particles are polyhedral in shape with somewhat smooth surface while the CMTKP-*g*-PAN shows polyhedral particles with needle shaped structures which on observing for surface morphology at higher resolution shows CMTKP particles intertwined with PAN particles.

The results (Table 2) of swelling study of CMTKP-*g*-PAN reveal that graft copolymer shows pH dependent swelling behaviour, with higher swelling in acidic and alkaline pH while lesser swelling at pH approaching neutrality. It can be explained by the fact that the graft copolymer comprises of CMTKP (anionic gum) and PAN (cationic polymer), at acidic pH the cationic PAN ionizes while at alkaline pH the anionic CMTKP ionizes, as a result it shows pH dependent swelling behaviour.

4. Conclusion

Optimization of synthesis of graft copolymer of carboxymethyl tamarind seed polysaccharide and polyacrylonitrile was studied employing 4-factor, 3-level central composite experimental design. Increasing the concentration of acrylonitrile decreased the grafting efficiency while variation in ammonium persulphate concentration showed a synergistic influence. Further, grafting of poly(acrylonitrile) on carboxymethyl tamarind seed polysaccharide improved the thermal stability, increased the crystallinity and imparted pH dependent swelling characteristics. The results indicate potential usefulness of graft copolymer in designing pH-responsive applications.

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