DOI: 10.1002/masy.200950313

Polyacrylamide Grafted Carboxymethyl Tamarind (CMT-g-PAM): Development and Application of a Novel Polymeric Flocculant

*Gautam Sen, Sagar Pal**

Summary: Water is scarce commodity now. Recycling of municipal wastewater, industrial and mineral processing effluents require treatment with the inorganic or organic flocculants. Both synthetic and natural polymers are used as flocculants. Natural polymers are biodegradable and are effective at very large dosages but are very shear stable. The synthetic polymers are highly effective flocculants at very small dosages and have high tailorability, but have poor shear stability. In the authors' laboratory, a novel polymeric flocculant has been developed by grafting polyacrylamide onto the backbone of carboxymethyl tamarind (CMT-g-PAM). Various grades were developed to optimize the best flocculant. The grafted polymers were characterized by various characterization techniques such as intrinsic viscosity measurement, FTIR spectroscopy, ^{13}C-NMR spectroscopy, elemental analysis etc. The flocculation studies were carried out using turbidity test as well as settling test. The optimized CMT-g-PAM was then compared with some of the commercial flocculants available in national and international markets in colloidal suspensions and it has been found that our synthesized flocculant surpasses most of the commercial flocculants in performance.

Keywords: flocculant; grafting; polyacrylamide

Introduction

Fresh water is a scarce commodity now. Recycling of domestic wastewater, industrial effluents and mineral processing effluents has been accepted by the application of synthetic flocculants for solid-liquid separation due to economic and environmental considerations all over the world.[1–3] When polymers are involved in a solid-liquid separation by an aggregation process of colloidal particles, the process is termed as flocculation.[4] In general, the flocculation is caused by the addition of minute quantity of chemicals, known as 'flocculants'. Both inorganic and organic flocculants are used in various kinds of flocculation phenomenon.[5] Among the inorganic flocculants, the salt of multivalent metals like aluminium and iron are mostly used. The organic flocculants are essentially polymeric in nature.

Among the polymeric flocculants, the synthetic polymers can be tailor made by controlling the molecular weight, molecular weight distribution, and chemical structure of polymers, nature and ratio of the functional groups on the polymeric backbone. Due to versatile tailorabiltiy, synthetic polymers are very efficient flocculants. However, they are not biodegradable and shear resistant. Natural polymers mainly polysaccharides, are moderately efficient due to their low molecular weights, are shear stable, biodegradable, cheap and easily available from reproducible farm and forest resources.[4,6] The biodegradability of natural polymers reduces their shelf life and

---

Department of Applied Chemistry, Birla Institute of Technology, Mesra (BIT-Mesra), Ranchi – 835 215, Jharkhand, India
Fax: +91-651-2275401;
E-mail: sagarpal@bitmesra.ac.in

needs to suitably controlled.[7] It is evident that all polymers, be it natural or synthetic, have one or more disadvantages.[8]

In the past, several attempts have been made to combine the best properties of both by grafting synthetic polymers onto the backbone of natural polymers.[9–14] One of the greatest advantages gained is the consequent reduced biodegradability because of a drastic change in the original regular structure of the natural polymer as well as the increased synthetic polymer content within the product. It is also observed that the grafting of shear degradable polymers onto a rigid polysaccharide backbone provides fairly shear stable systems.[15,16]

Ceric ion has been used to initiate graft copolymerization of many monomers on various substrates.[17–21] Grafting is generally considered to result from propagation of radical sites generated on polymeric substrates and therefore, minimizes the formation of homopolymer.

Further, the acrylamide and ceric ion concentrations are kept below 2.0 M within the limits of Owen and Shen;[22] it ensures proper grafting and absence of homopolymerization.

It has been observed that by grafting flexible polyacrylamide chains onto polysaccharides, it is possible to develop efficient, shear stable and controlled biodegradable flocculants for the treatment of industrial effluents and mineral processing. In these flocculants, the flexible chains of polyacrylamide are grafted onto rigid polysaccharide backbone. Hence the approachability of polyacrylamide chains to metallic and non-metallic contaminants increases significantly. Thus, they are endowed with highly efficient attributes (Singh's Easy Approachability Model).[1,7,8,23–26] This model has been proved qualitatively as well as quantitatively.[27]

Tamarind kernel polysaccharide (TKP) is a naturally occurring polysaccharide. Carboxymethyl tamarind (CMT) has been synthesized by reacting TKP with sodium salt of monochloroacetic acid (SMCA) in presence of sodium hydroxide (NaOH).[28]

Graft copolymers based on polysaccharides and polyacrylamides have been synthesized in recent years. However, no attempt have been made to synthesize polyacrylamide grafted CMT and to test their efficacies as flocculants. The present paper outlines the detailed synthesis of polyacrylamide grafted CMT, their optimization, thorough characterization by using various materials characterization techniques and their application as novel polymeric flocculants.

Experimental Part

Materials

Materials for Synthesis

Tamarind kernel polysaccharide was a gift sample from Hindustan Gum & Chemicals Ltd., Bhiwani, Haryana, India. Acrylamide was procured from E. Merck, Germany. Ceric ammonium nitrate was purchased from Loba Chemie, Mumbai, India. Acetone and hydroquinone were supplied by S. D. Fine Chemicals, Mumbai, India. All the chemicals were used as received without further purification.

Materials for Flocculation

Kaolin was purchased from Jyoti Chemicals, Mumbai, India. The suspension zeta potential of the kaolin is – 4.35.

Flocculants

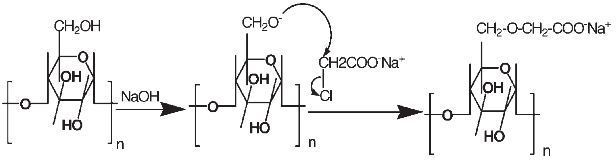
Two commercial flocculants namely Magnafloc LT 27 (anionic in nature) and Rishfloc 440 HV (anionic in nature) were used for comparison.

Synthesis

CMT has been synthesized by using TKP and sodium salt of monochloroacetic acid (SMCA) in presence of NaOH as depicted in Scheme 1.[28]

Grafting reaction was carried out by ceric ion induced redox initiation method.[17–21] The details of the synthesis and the reaction conditions are as follows:

1g of CMT was dissolved in 250 ml of distilled water with constant stirring and



Scheme 1.
Synthesis of CMT from TKP.

bubbling of a slow stream of nitrogen for about 15 minutes. Desired quantity of acrylamide was dissolved in 100 ml of distilled water and mixed with the CMT solution. Then oxygen free nitrogen was purged through the solution mixture for 35 minutes. At this stage, 25 ml of ceric ammonium nitrate (CAN) solution was added and accordingly nitrogen gas purging was continued for another 10 minutes. The reaction was continued for 24 hrs, after which it was terminated by adding saturated solution of hydroquinone. At the end of the reaction, the polymer was precipitated by adding excess of acetone. It was the dried in a vacuum oven. Subsequently it was pulverized and sieved. The reaction temperature was maintained at 28 ± 1 °C. The synthesis parameters are summarized in Table 1.

Purification of the Graft Copolymer by Solvent Extraction Method

The extraction of occluded PAM was carried out by solvent extraction using a mixture of formamide and acetic acid (1:1 by volume) [29]. The detailed procedure has been depicted in Scheme 2.

Characterization

Intrinsic Viscosity Measurement

Viscosity measurements of the polymer solutions were carried out with an Ubbelodhe viscometer (CS/S: 0.003899) at 25 °C. The viscosities were measured in dilute aqueous solutions. The pH of the aqueous solution was neutral. The time of flow for solutions was measured at four different concentrations. From the time of flow of polymer solutions (t) and that of the solvent (t_0, for distilled water), relative viscosity ($\eta_{rel} = t/t_0$) was obtained. Specific viscosity was calculated from the relation $\eta_{sp} = \eta_{rel} - 1$. Then, the reduced viscosity (η_{sp}/C), and the inherent viscosity ($\ln \eta_{rel}/C$) were calculated, where C is the polymer concentration in g/dL. The intrinsic viscosity was obtained from the point of intersection after extrapolation of two plots [30], i.e. η_{sp}/C versus C and $\ln \eta_{rel}/C$ versus C, to zero concentration (as shown in Figure 1).

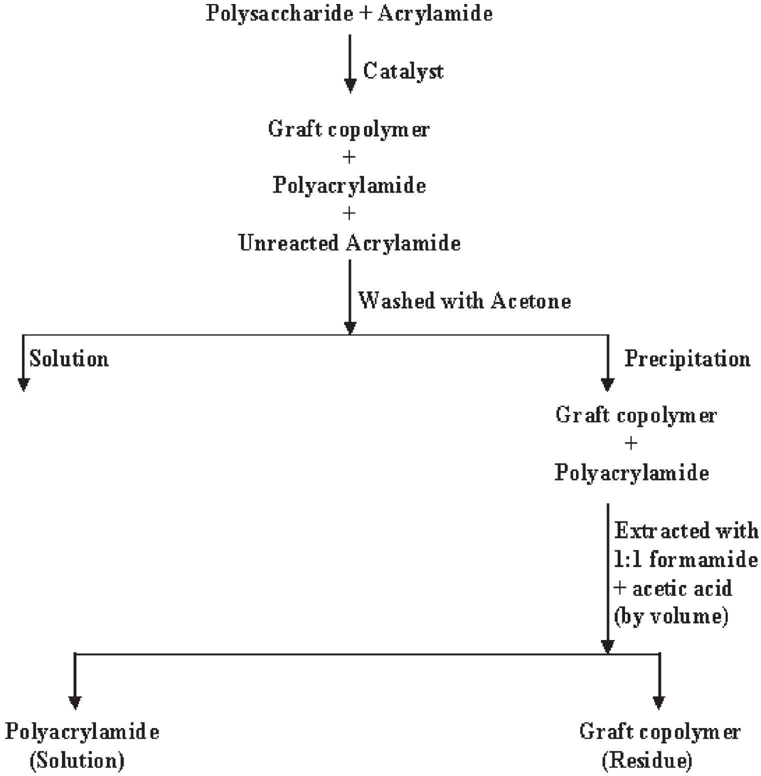
Elemental Analysis

The elemental analysis was undertaken with an Elemental Analyzer (Make – M/s Elementar, Germany; Model - Vario

Table 1.
Synthetic details of CMT-g-PAM.

Polymer	Amount of CMT (g)	Amount of AM (g)	Amount of CAN (g)	Temp. (°C)	% Grafting[a)]	Intrinsic viscosity (dL/g)
CMT-g-PAM 1	1	10	0.01	40	19	3.61
CMT-g-PAM 2	1	10	0.02	40	40	5.6
CMT-g-PAM 3	1	10	0.05	40	25	4.02
CMT-g-PAM 4	**1**	**15**	**0.02**	**40**	**50**	**7.4**
CMT-g-PAM 5	1	20	0.02	40	43	6.2
CMT	–	–	–	–	–	2.06

a)$\% \text{ of grafting} = \frac{\text{Amount of graft copolymer} - \text{Amount of Polysaccharide}}{\text{Amount of Polysaccharide}} \times 100$



Scheme 2.
Purification of graft copolymer.

EL III). The estimation of four elements, which is carbon, hydrogen, nitrogen and oxygen, was undertaken. The results have been summarized in Table 2.

FTIR Spectroscopy

The FTIR spectrums of CMT (Figure 2a) and CMT-g-PAM (Figure 2b) was plotted out using FTIR spectrophotometer (Model IR-Prestige 21, Shimadzu Corporation, Japan).Potassium bromide (KBr) pellet method was used for FTIR study.

Determination of Weight Average Molecular Weight by SLS Analysis

The weight average molecular weight (M_w) of CMT and various grades of CMT-g-PAM was determined by static light scattering (SLS) analysis using Light Scattering Spectrophotometer, (Model Nano ZS) made by Malvern Inst., UK. The results are summarized in Table 3.

NMR Spectroscopy

^{13}C-NMR spectroscopy of carboxymethyl tamarind (CMT) (Figure 3a), Polyacrylamide (PAM) (Figure 3b) and CMT-g-PAM 4 (Figure 3c) was recorded at 300 MHz with a Bruker 300P spectrometer.

Scanning Electron Microscopy

CMT (Figure 4a), PAM (Figure 4b) and CMT-g-PAM 4 (Figure 4c) was analyzed in scanning electron microscopy (SEM) in powdered form. JSM-6390LV Scanning Electron Micrograph (Jeol, Japan) was used for the above study.

Flocculation Characteristics

Flocculation tests of kaolin suspensions were carried out by using turbidity test and settling test.

A suspension of kaolin (0.25%; prepared by mixing 1 g in 400 ml. of distilled water) was used for flocculation study. The

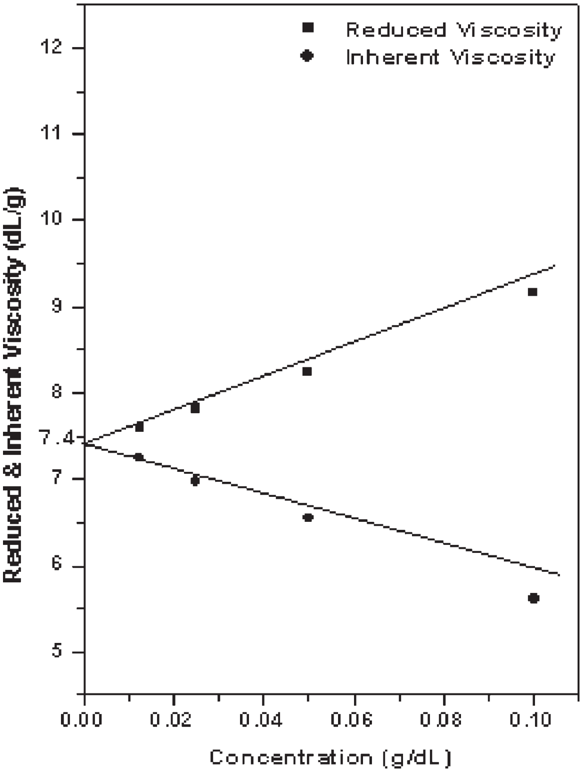


Figure 1.
Reduced and inherent viscosity versus concentration curves for the measurement of intrinsic viscosity of CMT-g-PAM 4.

suspension was taken in a 1-L beaker and the flocculant was added in solution form. The following procedure was uniformly applied to all the suspensions. Immediately after the addition of flocculant, the suspension was stirred at a constant speed of 60 rpm for 5 minutes. The flocs were then allowed to settle down during 10 minutes. At the end of the settling period, the turbidity of the supernatant liquid was measured. The dose of flocculants was varied from 0.025 to 1 ppm, calculated with respect to the total weight of the solution. The results are shown in Figure 5 and 6.

Settling test employs a 100 ml. stoppered graduated cylinder and stopwatch. The polymer solution was added to a suspension sample taken in the cylinder. The cylinder was turned upside down 10 times for thorough mixing. After that the cylinder was set upright, and the height of interface between water and settling solid bed is measured over time. The results are shown in Figure 7.

Table 2.
Elemental analysis results.

Polymer	%C	%H	%N	%O
CMT	38.48	9.017	1.176	51.327
CMT-g-PAM 1	38.07	7.16	11.10	43.20
CMT-g-PAM 2	37.7	7.01	12.15	43.05
CMT-g-PAM 3	36.12	7.28	12.01	43.82
CMT-g-PAM 4	**36.01**	**6.78**	**13.30**	**43.36**
CMT-g-PAM 5	36.42	6.51	13.34	43.00

Results and Discussions

Synthesis and Intrinsic Viscosity

The details of the graft copolymerization reaction and the percentage of grafting calculated are given in Table 1. In the present investigation, two series of grafted

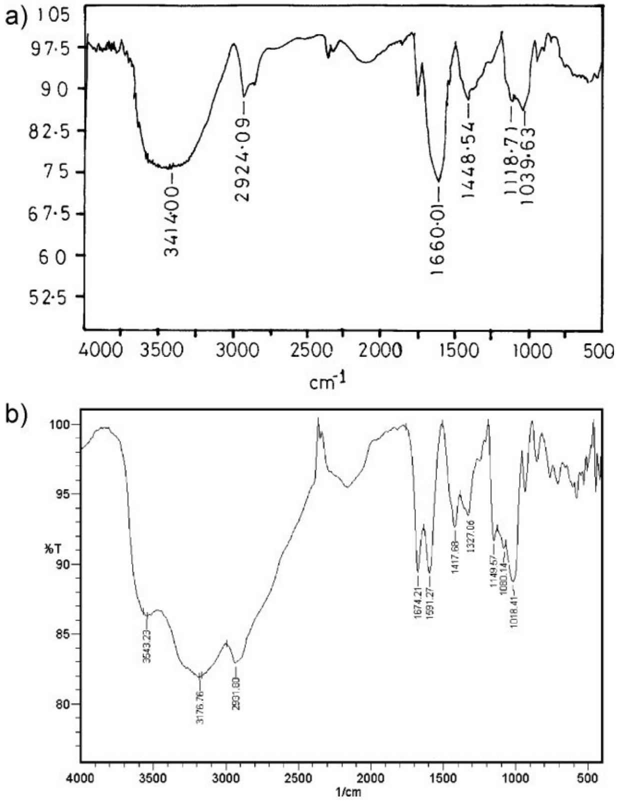


Figure 2.
(a) FTIR spectrum of CMT. (b) FTlR speclrum of CMT-g-PAM 4.

copolymers of CMT and PAM have been synthesized by grafting polyacrylamide onto CMT using ceric ion initiator. In the 1st series (1-3), the catalyst concentration was varied by keeping the concentration of CMT and AM constant. In the 2nd series (4–5), the acrylamide concentration was varied at a fixed CMT and catalyst concentration. The mechanism of ceric ion initiation involves the formation of chelate complex[29] that decomposes to generate free radical sites on the polysaccharide backbone. These active free radicals in presence of acrylic monomers generate graft copolymers. The average number of grafting sites per backbone molecule depend on the ratio of ceric ion concentration to CMT. A relatively low concentration of catalyst will initiate few grafting sites, resulting in long PAM chains against shorter PAM chains at high concentration. This is reflected in their corresponding viscosity values.

Table 3.
Determination of weight average molecular weight (M_w) by SLS analysis.

Polymer	Wt. Avg. Mol. Wt (Mw) (g/mole)
CMT	9.14×10^5
CMT-g-PAM 1	25.12×10^5
CMT-g-PAM 2	30.05×10^5
CMT-g-PAM 3	29.8×10^5
CMT-g-PAM 4	**40.15×10^5**
CMT-g-PAM 5	37.50×10^5

Intrinsic viscosity of a polymer is a measure of its hydrodynamic volume in solution, which in turn depends upon its molecular weight, structure, nature of solvent and temperature of the medium. For two polymers of approximately similar molecular weight, the branched polymer will have the lower hydrodynamic volume compared to its linear counter part and thus have lower intrinsic viscosity value.

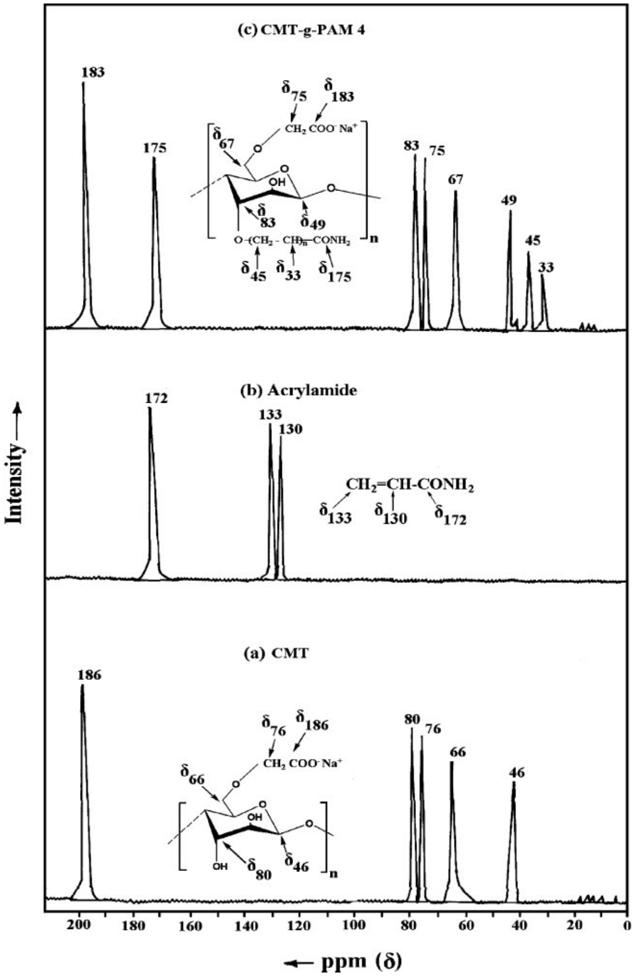


Figure 3.
^{13}C NMR spectroscopy of (a) CMT, (b) acrylamide and (c) CMT-g-PAM 4.

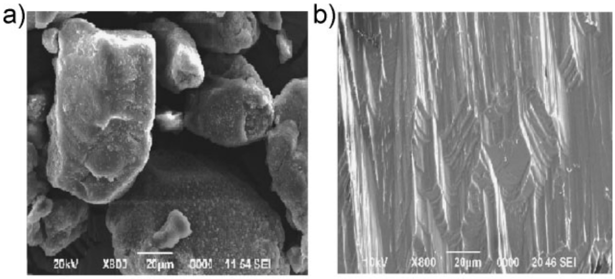
Further, in the case of branched polymers, the longer is the branching, the higher will be its intrinsic viscosity and vice-versa. This has been observed in practice (Table 1).

Elemental Analysis

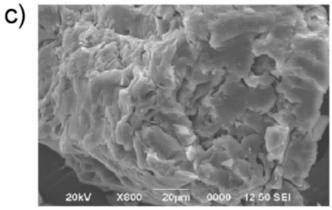
The results of elemental analysis of CMT and all the grades of CMT-g-PAM are listed in Table 2. CMT does not show any significant presence of nitrogen. However, the negligible amount of nitrogen may be due to the trace quantities of unisolated proteins in the polysaccharide. It has been found that there is a considerable percentage of nitrogen in the graft copolymers, which can be accounted to the presence of grafted PAM chains. In the series of graft copolymers, based on CMT, the variation in the nitrogen content, although not much, is significant in case of CMT-g-PAM 5. The higher percentage of nitrogen may be due to the increased polyacrylamide (PAM) content in the graft copolymer.

FTIR Spectra

The FTIR spectra of CMT and CMT-g-PAM 4 are shown in Figure 2a and b respectively. It can be seen (Figure 2a) that a broad absorption band in CMT at 3414 cm^{-1} is due to the stretching frequency of –OH groups. The bands around 1118 cm^{-1} and 2924 cm^{-1} are assigned to



SEM micrograph of CMT **SEM micrograph of PAM**



SEM micrograph of CMT-g-PAM 4

Figure 4.
SEM micrographs. (a) SEM micrograph of CMT; (b) SEM micrograph of PAM; (c) SEM micrograph of CMT-g-PAM **4**.

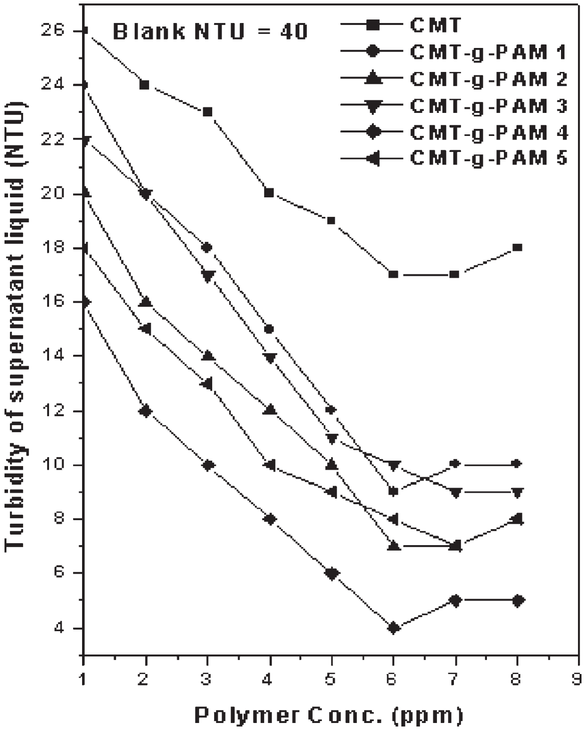


Figure 5.
Turbidity test in 0.25 wt% kaolin suspension using CMT and various grades of grafted CMT as flocculants.

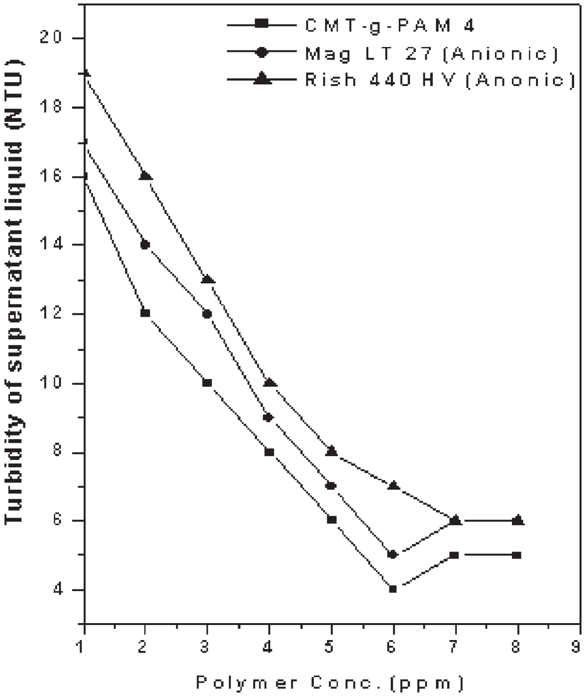


Figure 6.
Turbidity test in 0.25 wt% kaolin suspension using CMT-g-PAM 4 and commercial flocculants.

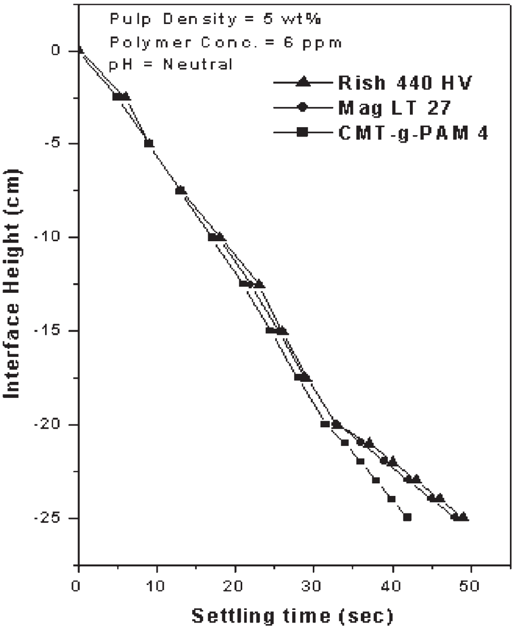


Figure 7.
Settling characteristics of kaolin suspension using CMT-g-PAM 4 and commercial flocculants.

–CO as well as –C–H stretching respectively. A strong band around 1039 cm^{-1} is due to CH_2–O–CH_2 stretching. Two additional peaks, one at 1660 cm^{-1} and other at 1448 cm^{-1}, are assigned for the $–COO^-$ groups.

In case of CMT-g-PAM 4, apart from the above mentioned peaks, there are three additional peaks, at 3176 cm^{-1} is for –NH stretching, 1327 cm^{-1} for –CN stretching and 1674 cm^{-1} for amide carbonyl group which clearly indicated that PAM has been grafted onto CMT backbone.

Weight Average Molecular Weight using SLS Analysis

The weight average molecular weight of CMT and various grades of CMT-g-PAM were determined from Debye Plot using SLS analysis. The results are summarized in Table 3. From Table 3, it is clear that the weight average molecular weight (M_w) of grafted polymers has increased drastically compared to CMT, which can be explained on the basis of the grafting of PAM onto the backbone of base polysaccharide (i.e. CMT). Again in case of various graft copolymers, CMT-g-PAM 4, which is optimized one (w.r.t. intrinsic viscosity and flocculation study), is having highest molecular weight, which is because of the longer PAM branches.

^{13}C-NMR Spectroscopy

It has been shown from Figure 3a (i.e ^{13}C-NMR for CMT) that CMT has five distinct peaks in the ^{13}C-NMR spectrum. The absorption peak at $\delta = 46$ ppm was for anomeric carbon atom and the peak at $\delta = 80$ ppm is for carbon atoms connected by –OH groups (i.e the carbon atoms in the six membered ring except anomeric carbon atom) and another peak at $\delta = 66$ ppm is attributed for the carbon atom of CH_2OH group as shown in Figure 3a. Apart from the peaks present at CMT, there is additional peaks at $\delta = 76$ ppm which is for the carbon atom of –O–CH_2– of the inserted carboxymethyl group and another peak at $\delta = 186$ ppm is for the carboxyl carbon atom of $–COO^-Na^+$.

Figure 3b shows the ^{13}C-NMR spectrum of acrylamide. Acrylamide had three major peaks in the spectrum. The peak at $\delta = 172$ ppm was for the amide carbonyl carbon. Peaks at $\delta = 130$ and $\delta = 133$ ppm were for two sp^2 hybridized carbon atoms (i.e. CH_2=CH–). These are shown in Figure 3b.

The ^{13}C-NMR spectrum of one of the graft copolymers (CMT-g-PAM 4) is shown in Figure 3c. The peak at $\delta = 183$ ppm was for the carboxyl carbon of $–COO^-Na^+$, which was present in CMT spectrum at $\delta = 186$ ppm. The peak at $\delta = 175$ ppm is for the carbon atom of $–CONH_2$ group. The peak at $\delta = 75$ ppm is for the carbons with the secondary hydroxyl groups and the peak at $\delta = 45$ ppm and $\delta = 33$ ppm was for the CH_2–CH_2 groups those were formed during the polymerization reaction.

As seen in ^{13}C NMR spectrum of the graft copolymer and acrylamide, acrylamide had two peaks at $\delta = 130$ and 133 ppm for two sp^2 hybridized carbon atoms, which were absent in the graft copolymer. Moreover, two additional peaks are present for graft copolymer at $\delta = 45$ ppm and $\delta = 33$ ppm, which is for the sp^3 hybridized carbon atoms (i.e. –CH_2–CH_2– units in the graft copolymer). Neither the CMT nor the Acrylamide spectrum had this peak. So, the absence of peak at $\delta = 130$ and 133 ppm and the presence of a peak at $\delta = 45$ ppm and $\delta = 33$ ppm is clear evidence of the grafted polyacrylamide chains onto the backbone of CMT.

Scanning Electron Microscopy

Figure 4a–c show the scanning electron micrographs of CMT, PAM and CMT-g-PAM 4. A careful examination of the micrographs reveals that a large difference in the morphological appearance of the polymers. CMT has a granular structure, which changed drastically from granular to fibrillar structure when PAM was grafted into CMT. This observation also supported the grafting of acrylamide onto CMT.

Flocculation Characteristics

The flocculation performance of CMT and all the graft copolymers was compared in 0.25 wt% kaolin suspensions. The result is shown in Figure 5. In this case, the turbidity of the supernatant liquid after flocculation was plotted against the polymer concentration. It is obvious from these results that CMT-g-PAM 4, which is having higher molecular weight and longer PAM branches is a better flocculant in kaolin suspension than that the other grafted polymers and CMT.

An attempt has been made to compare the flocculation characteristics of the best performing grafted polymer (CMT-g-PAM 4) with some of the commercially available flocculants in kaolin suspensions. From Figure 6, it can be concluded that CMT-g-PAM 4 dominates over both the commercial flocculants. Its performance is better than that of other commercial flocculants because the kaolin particles have slightly negative charges (suspension zeta potential = −4.2) and in this case, it appears that the grafting along with easy approachability of longer PAM branches of CMT-g-PAM 4 dominates the performance.

The settling tests were carried out in 5-wt% kaolin suspension. In this case, the settling time was plotted against the height of interface. Figure 7 shows the settling characteristics in kaolin suspension for CMT-g-PAM 4, Rish 440 HV and Mag LT27. It is clear from Figure 7 that CMT-g-PAM 4 is best flocculant while compared with the commercial flocculants.

Conclusion

From the above experimental investigations, it can be concluded that a novel polymeric flocculant has been developed by grafting polyacrylamide onto the backbone of carboxymethyl tamarind (CMT), which outperforms commercial flocculants available in national and international market at laboratory scale.

Acknowledgements: Authors are highly acknowledged for the financial support from Birla Institute of Technology, Mesra (BIT-Mesra), Ranchi, Jharkhand, India.

[1] R. P. Singh, G. P. Karmakar, S. K. Rath, N. C. Karmakar, S. R. Pandey, T. Tripathy, J. Panda, K. Kannan, S. K. Jain, N. T. Lan, *Polym Engg Sci* **2000**, *40*, 46.

[2] B. A. Bolto, *Prog Polym Sci* **1995**, *20*, 987.

[3] F. A. Rey, R. C. Varsanik, Applications and function of synthetic polymeric flocculants in waste water treatment., In: *Water soluble polymers beauty with performance*, J. E. Glass, Ed., American Chemical Society, Washington, DC **1986**.

[4] H. Barkert, J. Hartmann, Flocculants., in: *Encyclopedia of Industrial Chemistry*, 5th Edition, VCH, Weinheim **1988**, *11A*, 251.

[5] J. Bratby, *Coagulation and flocculation*, Uplands press, Cryodon, England **1980**.

[6] G. M. Moody, *Miner Engg* **1992**, *5*, 479.

[7] R. P. Singh, T. Tripathy, G. P. Karmakar, S. K. Rath, N. C. Karmakar, S. R. Pandey, K. Kannan, S. K. Jain, N. T. Lan, *Curr Sci* **2000**, *78*, 798.

[8] R. P. Singh, Hybrid flocculants aid water recycling, *Nature-News*, India, 3, **2000**.

[9] S. R. Deshmukh, R. P. Singh, *J Appl Polymer Sci*, **1991**, *43*, 1091.

[10] S. Ungeheur, H. W. Bewersdorff, R. P. Singh, *J Appl Polymer Sci*, **1989**, *37*, 2933.

[11] R. P. Singh, "Drag Reduction and Shear Stability Mechanisms". *Polymer flow Engg IP Chemisnoff* **1990**, *14*, 425.

[12] R. P. Singh, Advanced turbulent drag reduction and flocculating materials based on polysaccharides. In: *Polymers and other advanced materials, Emerging technologies and business opportunities*, P. N. Prasad, J. E. Mark, T. J. Fai, Eds., Plenum press, New York, 227.

[13] S. K. Rath, R. P. Singh, *J Appl Polymer Sci* **1997**, *66*, 1721.

[14] S. K. Rath, R. P. Singh, *Colloids and Surfaces* **1998**, *139*, 129.

[15] T. Tripathy, R. P. Singh, *Eup Polym J* **2000**, *36*, 1471.

[16] G. Mino, S. Kaizerman, *J Polym Sci* **1958**, *31*, 242.

[17] K. Beheri, K. Tunuk, M. Tripathi, *J. Appl. Polym. Sci.* **1999**, *71*, 739.

[18] R. L. Walrath, Z. Reyes, C. R. Russel, *Adv Chem* **1962**, *34*, 87.

[19] G. Mino, S. Kaizerman, E. Rasmussen, *J. Polym* **1959**, *39*, 523.

[20] G. F. Fanta, R. C. Burr, C. R. Russel, C. E. Rist, *J. Appl Polymer Sci* **1970**, *14*, 2601.

[21] F. D. Hartley, *J Polym Sci* **1959**, *34*, 394.

[22] D. R. Owen, T. C. Shen, In: "*Structure solubility relationships in polymers*", F. W. Harris, R. B. Seymour, Eds., Academic press, New York **1977**, 245.

[23] R. P. Singh, B. R. Nayak, D. R. Biswal, T. Tripathy, K. Banik, *Materials Research Innovations* **2003**, *7*, 331.
[24] R. P. Singh, Sagar Pal, D. Mal, *Macro. Symposia* **2006**, *242*, 227.
[25] Sagar Pal, D. Mal, R. P. Singh, *Colloids & Surfaces A: Physicochem & Engg. Aspects* **2006**, *289*, 193.
[26] S. Pal, D. Mal, R. P. Singh, *Carbohydrate Polymers* **2005**, *59*, 417.
[27] Witold Brostow, Sagar. Pal, Ram. P. Singh, *Materials Letters* **2007**, *61*, 4381.
[28] Sagar Pal, G. Sen, S. Mishra, R. K. Dey, U. Jha, *J. Appl. Polym. Sci.* **2008**, *110*(1), 392.
[29] G. F. Fanta, ''Synthesis of graft and block copolymers of starch''., In: *Block and Graft copolymerization*, Vol. *1*, R. J. Cerca, Ed., Wiley, New York **1973**, 11.
[30] E. A. Collins, J. Bares, F. W. Billmeyer, *Experiments in polymer science*, John Wiley & Sons, New York **1973**, p. 394.