https://doi.org/10.33451/florafauna.v29i1pp87-98
FLORA AND FAUNA ISSN 2456 - 9364 (Online)
2023 Vol. 29 No.1 PP 87-98 ISSN 0971 - 6920 (Print)

Microwave Assisted Synthesis and Characterization of *Pithecellobium dulce* Gum-Grafted-Polyacrylamide

***Harsh Kumar Garg[1], Praveen Singh[1], Niti Kushwaha[2], Ekta Pandey[3] and Sharat Srivastava[1]**

[1]Department of Chemistry,
[2]Department of Botany,
Dayanand Vedic College, ORAI-285001 (U.P.) INDIA
[3]Department of Chemistry, BIET,
JHANSI-284128 (U.P.) INDIA
*Corresponding Author
E-mail : dr.harshkumargarg2012@gmail.com

Received **:** 16.03.2023; ***Revision*** **:** 28.04.2023; ***Accepted*** : 08.05.2023

ABSTRACT

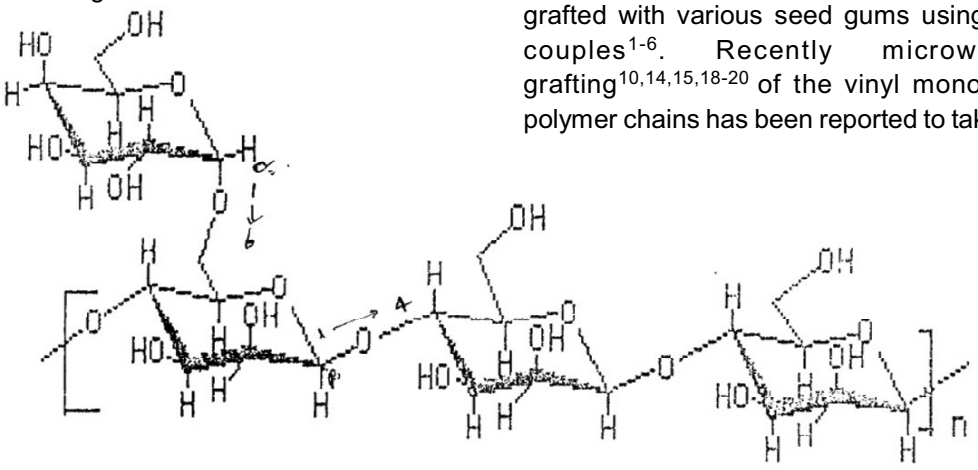
The isolation and spectral data of seed extracts in various solvents of *Pithecellobium dulce*(PD) was done. The synthesis of acrylamide-grafted gum and efficiency was carried out by microwave-assisted free radical polymerization using silver nitrate and ascorbic acid. A table of graft copolymers was prepared, varying in the amount of acrylamide, $AgNO_3$, thermal grafting & microwave irradiation time.FTIR and Chromatographic studies characterized these graft copolymers. Comparing grafting factors such as efficiency, percentage grafting and percentage conversion was carried out among various graft copolymers and then correlated with elemental analysis.

Figures : 04 References : 20 Tables : 04
KEY WORDS : Efficiency, Grafting, Microwave assisted synthesis,*Pithecellobium dulce*, Polysaccharides, Seeds dxtracts

Introduction

Grafting vinyl monomers onto naturally occurring polysaccharides significantly improves their properties. Graft copolymers of Starch/Xanthan/Guar gum exhibit much better flocculating characteristics than those of natural polysaccharides alone and with some synthetic polymer-based flocculating agents[11-13].

Cross-linkedGuar-g-polyacrylamide hydrogelmicrospheres[16] are used in water transport and drug release. Conventionally acrylamide has been grafted with various seed gums using various redox couples[1-6]. Recently microwave-promoted grafting[10,14,15,18-20] of the vinyl monomers onto the polymer chains has been reported to take place in good



Structure of the seeds gum from *Pithecellobium dulce*

ACKNOWLEDGEMENTS : Authors are thankful to the Head of Institution, Dayanand Vedic College, Orai for his support and encouragement.We also express lot of thanks to Director BIET Jhansi for spectral analysis and necessary laboratory facilities.

TABLE-1: Comparison of conventional thermal grafting and grafting under MW irradiation.

S. No.	Components	Conven. The method with a redox system and catalyst	Under MW without a redox system and catalyst
1	% Grafting	105	95
2	% Efficiency	42.17	38.15
3	Microwave power	-	80%
4	Temperature	35 ^{0}C	100 ^{0}C
5	Time	60 min	1.50 min
6	N-element test	positive	Positive

(At fixed conc. of PD gum (0.1 g/25 ml); Acrylamide (14x10^{-2} M/L) in MW method; PD gum (0.1 g/25 ml); Acrylamide (14 x 10^{-2} M/L) Ascorbic acid (2.3 x 10^{-2} M/L); $K_2S_2O_8$ (10 x 10^{-3} M/L); $AgNO_3$ (8.0 x 10^{-5} M/L) in Conventional method; total reaction volume 25 ml).

yield with the minimum use of the chemicals and in a short time. Due to the high utility of the Gum-grafted-polyacrylamide and the unavailability of any literature on the use of microwave irradiation for the grafting of the acrylamide onto the *Pithecellobium dulce* seed gum, in the present study, an attempt has been made to use microwave irradiation to graft polyacrylamide on to *Pithecellobium dulce* seed gum to get the optimal conditions with minimum use of chemicals.

Materials and Methods

The present study was conducted under the Chemistry department at Dayanand Vedic College (Orai), Bundelkhand region (U.P.). An LG (Model No. MC3283AG, 1300W, 230V, 50Hz) domestic microwave oven was used for all experiments. The average bulk temperature at the end of the reaction was measured by inserting a thermometer into the reaction mixture. All the experiments were done in the aqueous medium. I.R. spectra were recorded on a Brucker Vector-22 Infra-red spectrophotometer using KBr pellets. Acrylamide (E. Merck) was recrystallized twice in methanol (GR) and dried in a vacuum.

Ascorbic acid and Potassium persulfate were used without further purification. $AgNO_3$ was used as a catalyst. PD seed gum was used after purification. The percentage and efficiency of grafting were calculated using formula as follows[7].

$$\% \text{ Grafting (\%G)} = \frac{W_1 - W_0}{W_0} \times 100$$

$$\% \text{ Efficiency (\%E)} = \frac{W_1 - W_0}{W_2} \times 100$$

Where W_1, $W_{0,}$ and W_2 represent the weight of the grafted PD gum, the weight of the original PD gum, and the weight of the monomer used, respectively.

Purification of the *Pithecellobium dulce* seed gum

The following methods purified the crude of *Pithecellobium dulce* polysaccharide–

1. Multiple precipitations: -The dried crude PD gum was dissolved in distilled water (1.0 litre) containing 1% acetic acid with constant stirring. The solution was filtered and added very slowly in a thin stream to ethanol (5 litre) with continuous vigorous stirring and kept overnight. The precipitated polysaccharide was filtered, washed with ethanol, followed by absolute alcohol and dried. Dissolution and reprecipitation were repeated four times to get a white fibrous polysaccharide.
2. Deproteinization: -The PD gum obtained after repeated precipitation was dissolved as above. The aqueous solution was shaken well with chloroform in a separating funnel when the denatured proteins formed gel at the water chloroform interface. The mucilage layer was separated, and the procedure was repeated five times to remove the protein. Adding the aqueous layer to the significant excess of ethanol with stirring regenerated the mucilage.
3. Complexation with barium hydroxide solution: -The crude PD gum was purified through barium complexing by preparing a 2.5% (w/v) gum solution by continuous stirring for 18hours at 60 ^{0}Cand precipitating with a saturated barium hydroxide solution. The complex was separated by centrifugation and then suspended in 1 M acetic acid, stirred for 6 hours, centrifuged, precipitated with ethanol, and washed with ethanol to get a white fibrous polysaccharide.

TABLE-2: Effect of MW power and exposure time on %G and %E

(At fixed conc. of PD gum (0.1 g/25 ml), Acrylamide (14 x 10^{-2} M/L); Total reaction volume 25 ml)

S. No.	% MW	Exposure time in min.	Without redox couple/catalyst			
			Temp. ^{0}C	Yield	%G	%E
1	60%	0.50	71	135	35	14.06
		0.75	89	142	42	16.87
		1.00	94	150	50	20.08
		1.50	97	158	58	23.29
		2.00	100	167	67	26.91
2	70%	0.50	83	140	40	16.06
		0.75	95	146	46	18.47
		1.00	98	165	65	26.10
		1.50	100	171	71	28.51
		2.00	100	178	78	31.33
3	80%	0.50	92	154	54	21.69
		0.75	97	165	65	26.10
		1.00	100	185	85	34.14
		1.50	100	195	95	38.15
		2.00	100	175	75	30.12
4	90%	0.50	100	168	68	27.31
		0.75	100	182	82	32.93
		1.00	100	165	65	26.10
		1.50	100	155	55	22.09
		2.00	100	148	48	19.28
5	100%	0.50	96	179	79	31.73
		0.75	100	167	67	26.91
		1.00	100	158	58	23.29
		1.50	100	150	50	20.08
		2.00	100	139	39	15.66

Preliminary studies

The purified PD gum was a white amorphous material, lightweight, and hydrated slowly to form a viscous solution. Based on quantitative results, methoxyl[8], acetyl[9,] and uronide[17] contents were negligible. Further quantitative tests showed the absence of nitrogen, Sulphur, and halogen. Upon treatment with Fehling's solution, the PD gum formed an insoluble copper complex but did not reduce them, showing the absence of free-reducing sugars.

Examined free sugars by applying three spots of its solution in water on the strip of Whatman filter paper No. 42 (paper size 15 cm X 45 cm). The paper was developed in solvent 1-butanol-ethanol-water (5:1:4)for 40 hours separately, dried, and cut lengthwise into three strips, each containing one spot. The three strips were sprayed with three different reagents using naphthoresorcinol and trichloroacetic acid (give color with Ketoses only) on one, aniline hydrogen phthalate on the second, and silver nitrate in acetone, followed by ethanolic sodium hydroxide on the third. The first two papers were dried in an oven at 110^{0}C and the third was air-dried. None of the strips showed any spots; hence the PD gum contains no free sugars.

Grafting of the *Pithecellobium dulce* seed gum under microwave irradiation

A solution (total volume 25 ml) of PD gum (0.1g) and acrylamide (14x10^{-2} M/L) in water was irradicated in a domestic MW oven in a 150 ml flask. The reaction was repeated with different MW power, exposure time (Table-2), monomer concentration (Table-3), and PD gum concentration (Table-4). The PD-grafted-poly(acrylamide) was separated from polyacrylamide by precipitating the reaction mixture with methanol: water (7:3), in which the homopolymer dissolves. Grafted gum

TABLE-3:Effect of Acrylamide Concentration on %G and %E

S. No.	Acrylamide Conc. (M/L)	Temp. ^{0}C	Yield (mg)	%G	%E
1	6×10^{-2}	95	125	25	23.45
2	8×10^{-2}	95	140	40	28.14
3	10×10^{-2}	97	161	61	34.46
4	12×10^{-2}	98	178	78	36.58
5	14×10^{-2}	100	195	95	38.15

(At 80% MW power, Exposure time was 1.50 min. and fixed conc. of PD gum 0.1 g/25 ml); Total reaction volume 25 ml)

TABLE-4: Effect of PD gum Concentration on % G and % E

S. No.	PD gum Conc. (g/L)	Temp. ^{0}C	Yield (mg)	%G	%E
1	2	98	135	170	34.14
2	4	100	195	95	38.15
3	6	100	225	50	30.12
4	8	100	268	34	27.31
5	10	100	305	22	22.09

(At 80% MW power, Exposure time was 1.50 min. and fixed conc. of Acrylamide (14×10^{-2} M/L); Total reaction volume 25 ml)

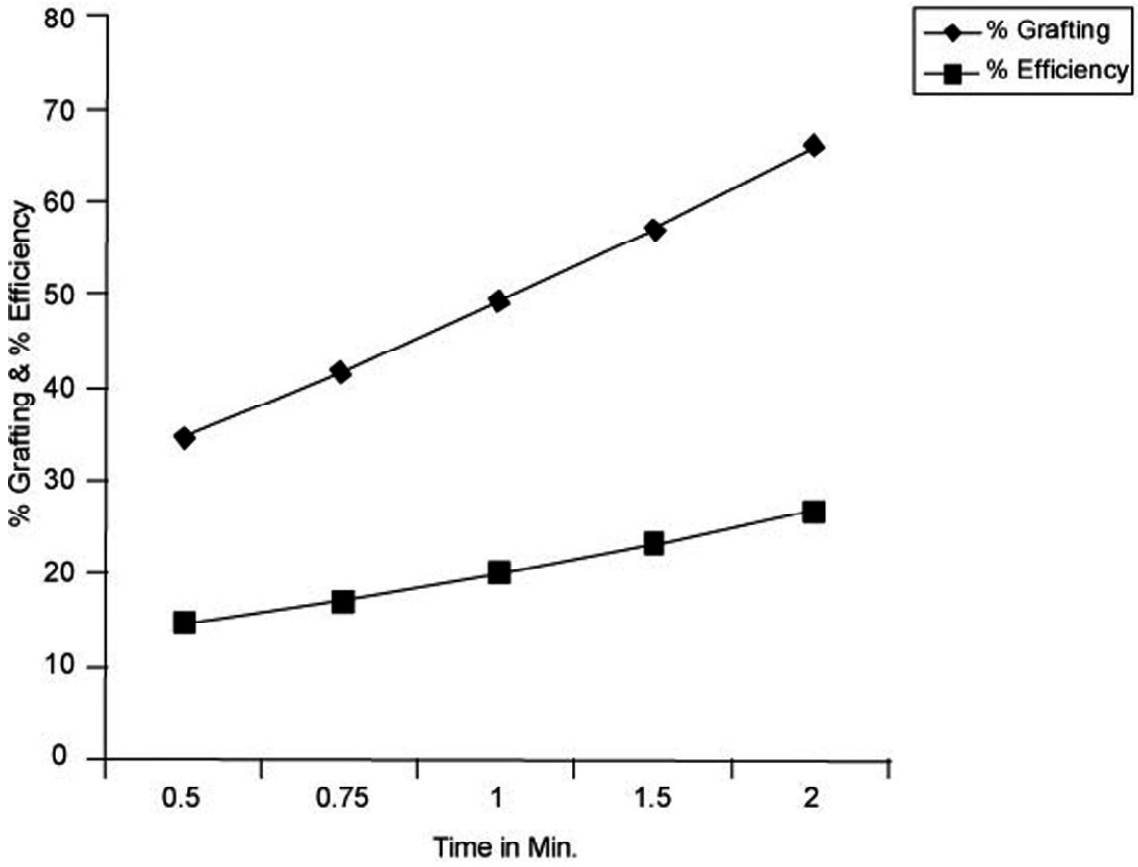


Fig. 1a: Effect of exposure time on % G and % E {At fixed conc. of seed gum (0.1 g/25ml.), Acrylamide (14 x 10 M/L), total reactior volume 25 ml at 60% MW power}

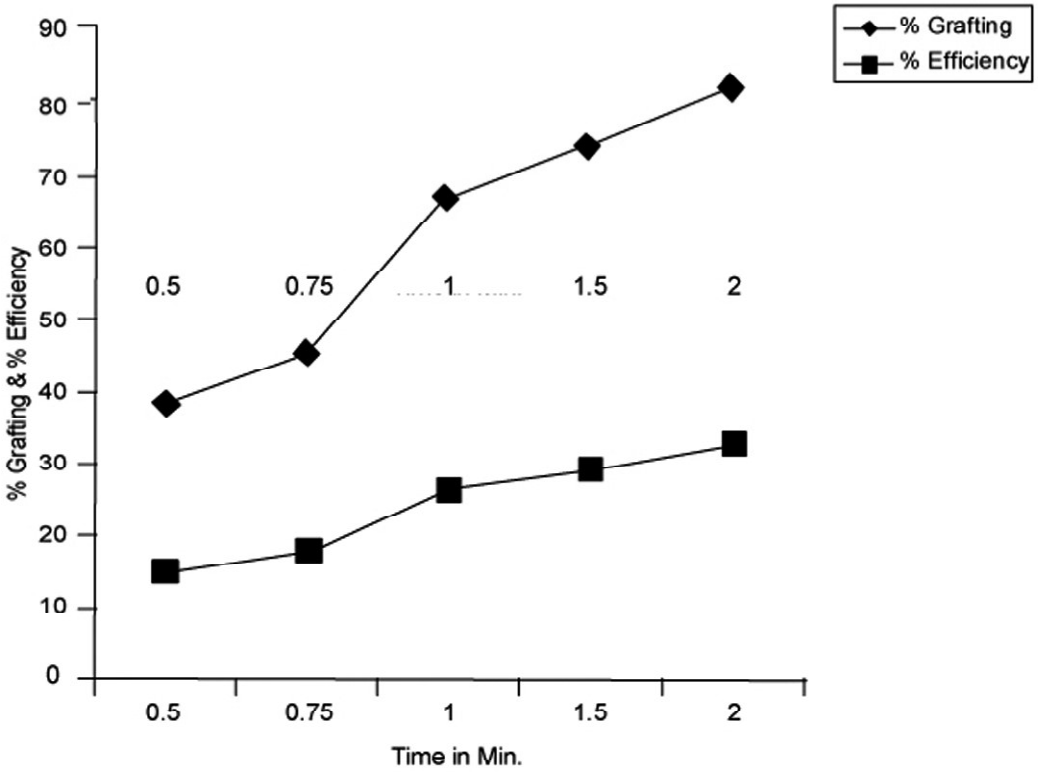


Fig. 1b: Effect of exposure time on % G and % E {At fixed conc. of seed gum (0.1 g/25ml.), Acrylamide (14 x 10 M/L), total reactior volume 25 ml at 70% MW power}

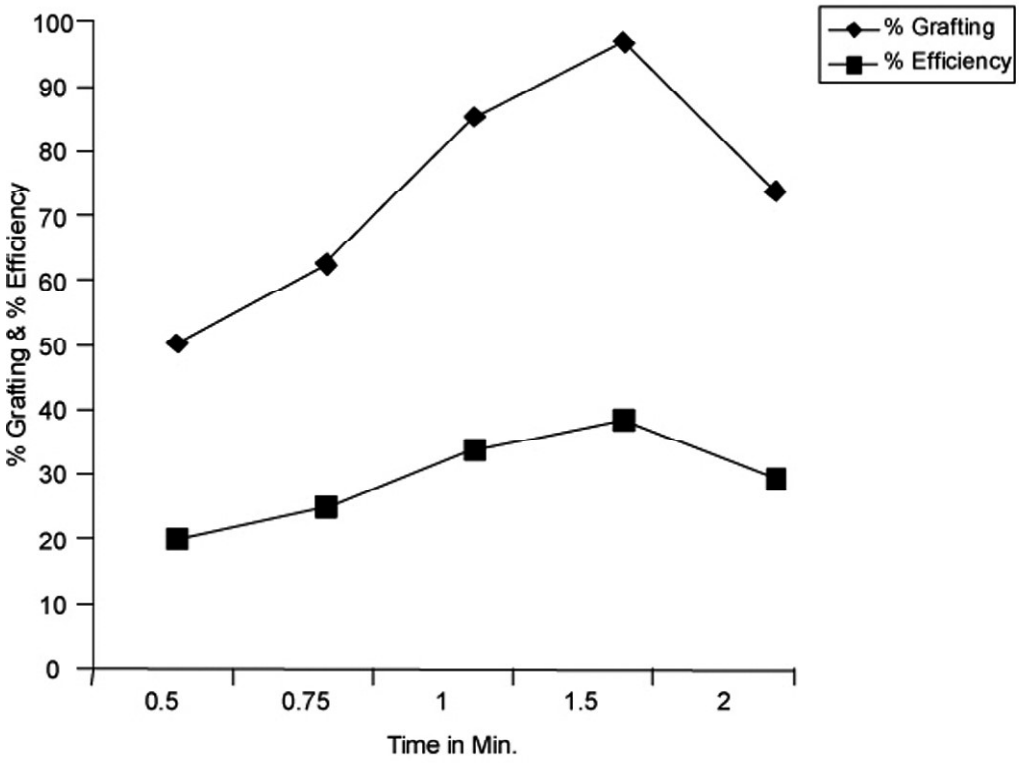


Fig. 1c: Effect of exposure time on % G and % E {At fixed conc. of seed gum (0.1 g/25ml.), Acrylamide (14 x 10 M/L), total reactior volume 25 ml at 80% MW power}

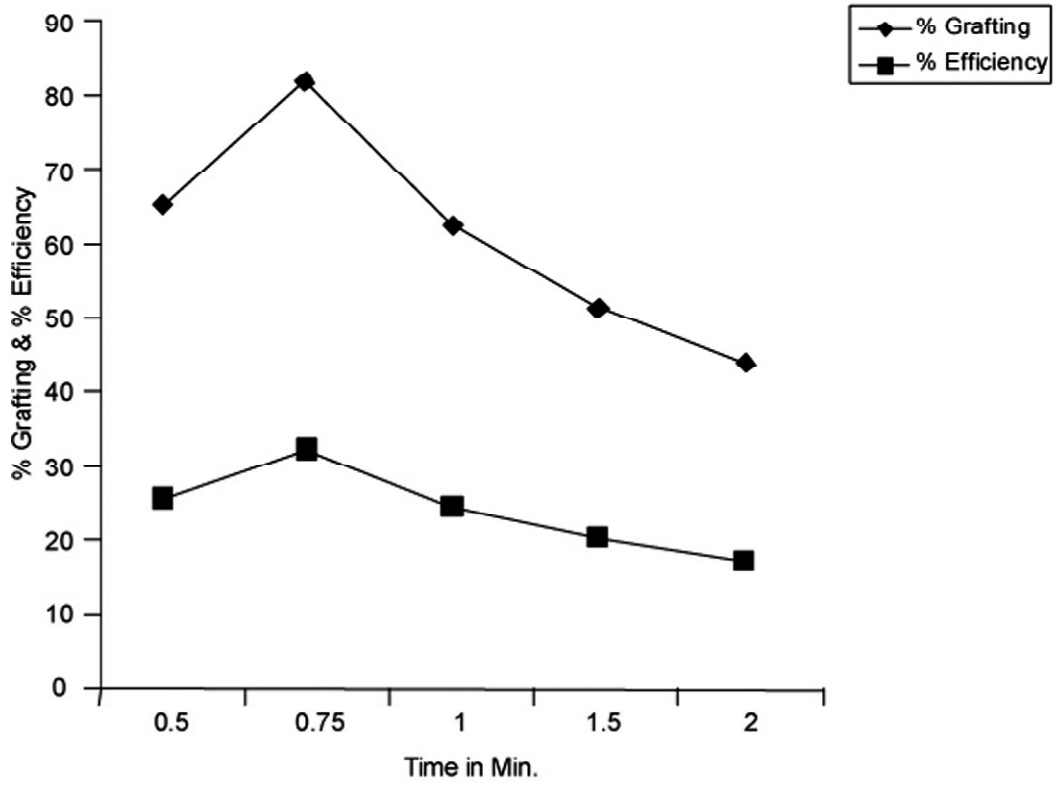


Fig. 1d: Effect of exposure time on % G and % E {At fixed conc. of seed gum (0.1 g/25ml.), Acrylamide (14 x 10 M/L), total reactior volume 25 ml at 90% MW power}

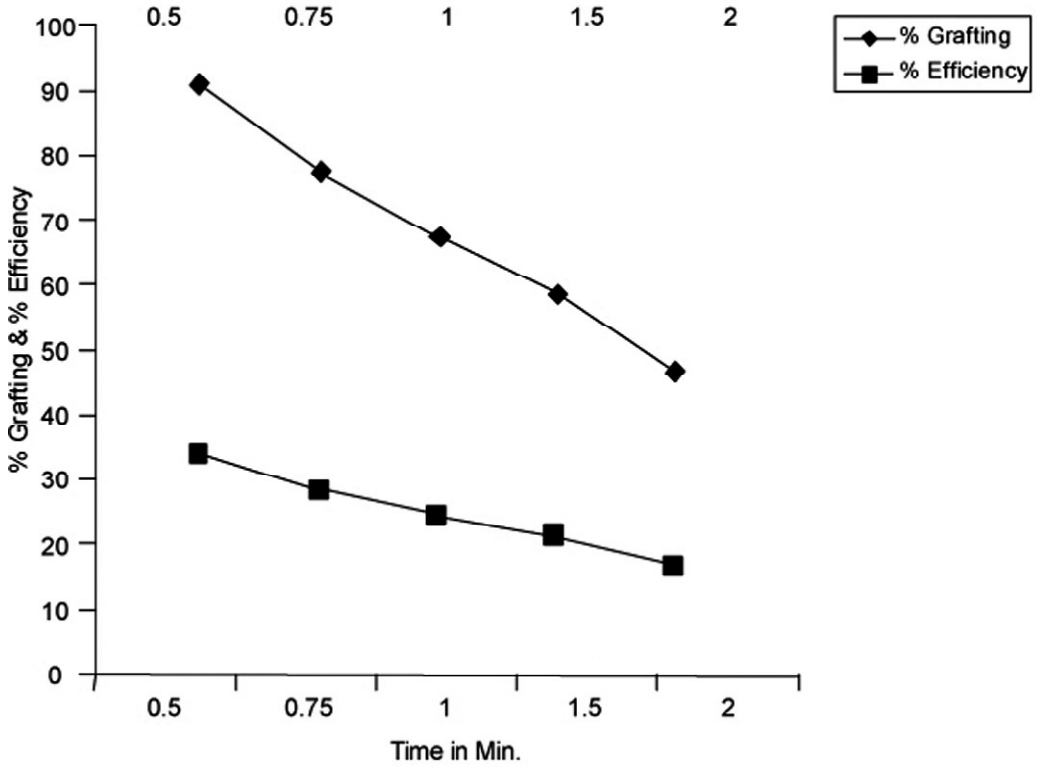


Fig. 1e: Effect of exposure time on % G and % E {At fixed conc. of seed gum (0.1 g/25ml.), Acrylamide (14 x 10 M/L), total reactior volume 25 ml at 100% MW power}

was repeatedly washed with methanol: water (7:3) and dried. % G and % E were calculated. The maximum grafting was observed at 80% MW power at 100 ^{0}C.

Grafting of the *Pithecellobium dulce* seed gum on a thermostatic water bath

A solution (total volume 25 ml) of PD gum (0.1 g), acrylamide (14 x 10^{-2} M/L), $AgNO_3$ (8.0 x 10^{-5} M/L), and ascorbic acid (2.3 x 10^{-2} M/L) water in a 150 ml conical flask was thermostatic at a temperature of 35.0+0.2 ^{0}C.After 30 min., $K_2S_2O_8$(10 x 10^{-3} M/L) was added, and this time of addition of persulphate was taken as zero time. The reaction was allowed to continue for one hour. Separation of PD-g-poly(acrylamide) from polyacrylamide was done as described above. % G 105 and % E 42.17.

Pithecellobium dulce seed gum was used after purification. Purification of the PD gum was done as follows –

(1) **Multiple precipitations or repeated precipitation:**

The crude gum was dissolved in 1% acetic acid and precipitated by adding the acid solution slowly to the excess of ethanol with continuous stirring. Dissolution and reprecipitation were repeated four times to get a white fibrous precipitate.

(2) **Deproteinization:**

The deproteinization of the *Pithecellobium dulce* seed gum was done by shaking the aqueous solution with chloroform. This method was repeated several times to remove most of the proteins.

(3) **Complexation with barium hydroxide solution:**

The deproteinized gum was purified by barium complexation. When dispersed in cold water, the pure, *Pithecellobium dulce* seed gum formed an opaque, viscous solution, which failed to reduce Fehling's solution.

Results and Discussions

Grafting of the *Pithecellobium dulce* seed gum:-

Under microwave (MW) irradiation, grafting of the acrylamide (AA) onto the *Pithecellobium dulce* seed gum (PD) in an aqueous medium was found to take place in the absence of any redox system and catalyst, with yields comparable to the thermal grafting with potassium persulphate/ascorbic acid in the presence of Ag^+ and atmospheric oxygen. Thus, the grafting under MW can only use inexpensive catalysts and redox systems. Under MW conditions, the grafting occurs in an environmentally friendly manner in an aqueous medium. As grafting occurs even withouta redox system/catalyst, increased grafting efficiency cannot be a mere thermal effect;instead, it is the MW effect. Conventionally, it was impossible to graft poly(acrylamide) onto PD gum withoutan initiator, even when the temperature was 100 ^{0}C.

Characterization of the grafted gum

PD-grafted-polyacrylamide (PD-g-PAA) was characterized by nitrogen element test and Infrared spectra.

(a) Nitrogen element test

It gives apositive nitrogen element test in the PD-g-PAA prepared by microwave procedure and synthesized by conventional thermal grafting method, confirming the grafting.

(b) FTIR Spectra

The infrared spectrum of pure PD gum had a strong broadband at 3410 cm^{-1}, a bond at 2900 cm^{-1} indicating –OH group, and C-H linkage, respectively, while the IR spectrum of PD-g-PAA had an absorption peak at 1632.38 cm^{-1} for >C=O stretching, N-H stretching peaks at 3363 cm^{-1} and 3210 cm^{-1} and C-N stretching at 1455 cm^{-1}.A physical blend of PD gum and PAA after selective removal of PAA with methanol: water (7:3) showed no absorption at 1680, 3350, and 3170 cm^{-1}. This substantiates the formation of the graft copolymer.

The effect of changing various parameters of the grafting reaction, *viz.* monomer concentration, PD gum concentration, MW power, and exposure time was studied to obtain the optimum grafting conditions.

1. Effect of Microwave power and exposure time

The % grafting (%G) and % efficiency (%E) were increased with the increase of MW power (Fig-1-5) and exposure time (Fig-6-10) in the beginning, but when MW power was more than 80%, grafting yields were lowered indicating higher microwave radiation promotes homopolymerization more, than the graft co-polymerization and due to formation of more homopolymer and the yield of grafted gum is reduced. When the more than 80% MW power, the % G observed was maximum at 1.5 min. Exposure time and any further increase in exposure time at the same MW power or above lowered the grafting yield indicating side reactions at higher MW power.

2. Effect of acrylamide

The % grafting and % efficiency were observed to increase with the increase in acrylamide concentration from 6.0-14.0 x 10^{-2} M/L. (Fig-11) This may be recognized due to two reasons-

(i) The formation of more polyacrylamide radicals generates more grafting sites.

(ii) The availability of different monomer molecules for the grafting.

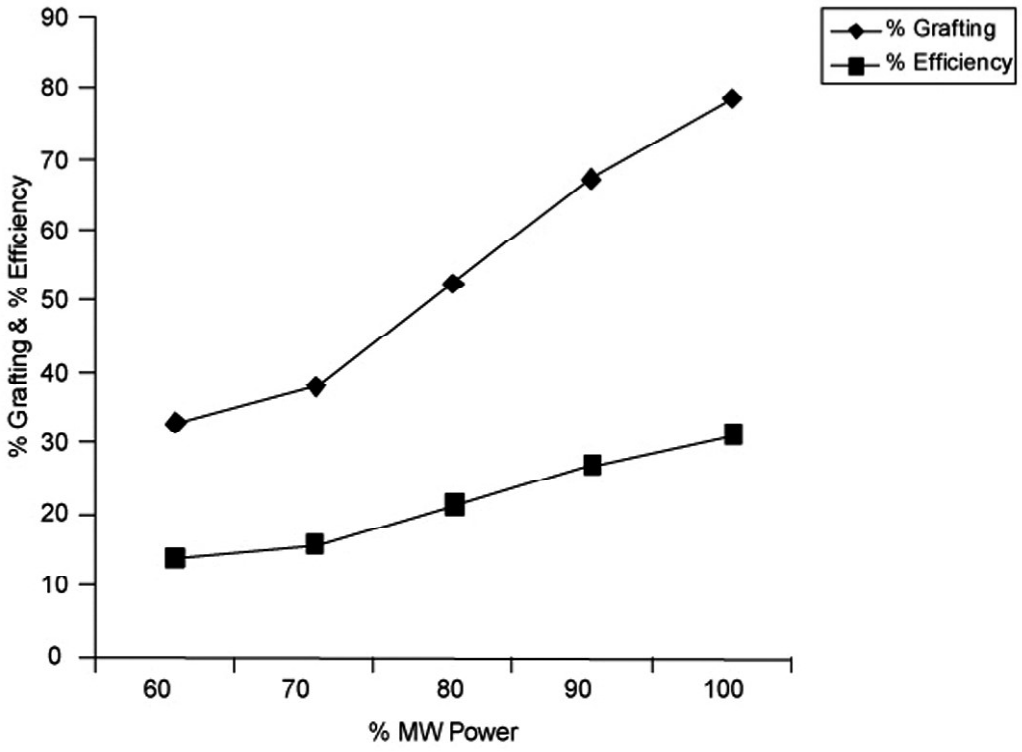


Fig. 2a: Effect of % MW Power on % G and % E {At fixed conc. of seed gum (0.1 g/25ml.), Acrylamide (14 x 10 M/L), total reactior volume 25 ml at 0.25 Min. exposure time}

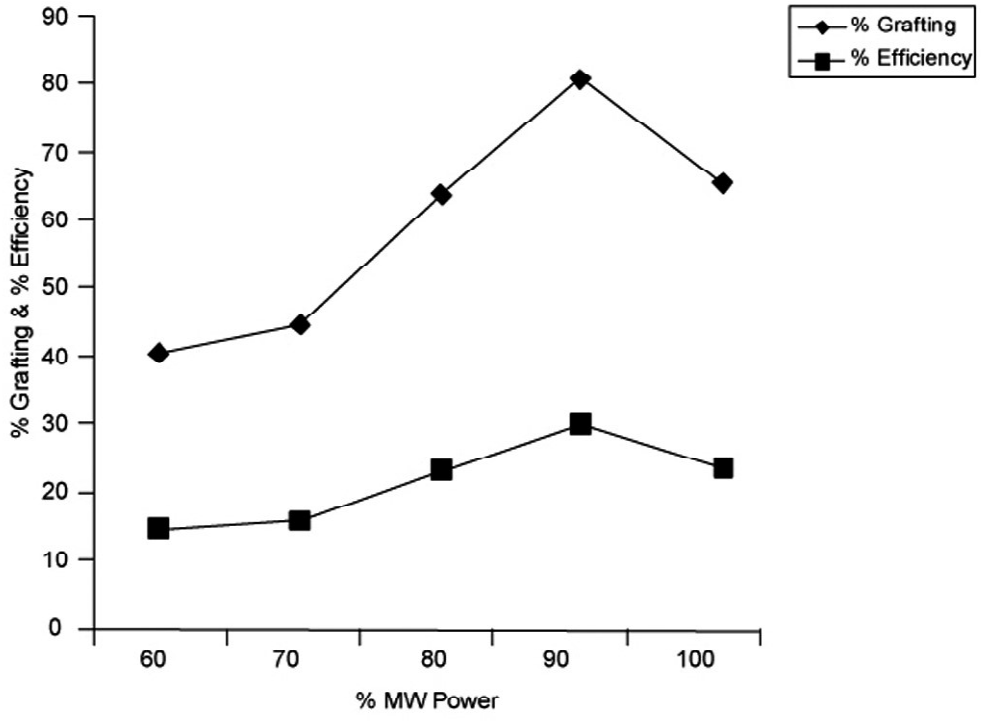


Fig. 2b: Effect of % MW Power on % G and % E {At fixed conc. of seed gum (0.1 g/25ml.), Acrylamide (14 x 10 M/L), total reactior volume 25 ml at 0.75 Min. exposure time}

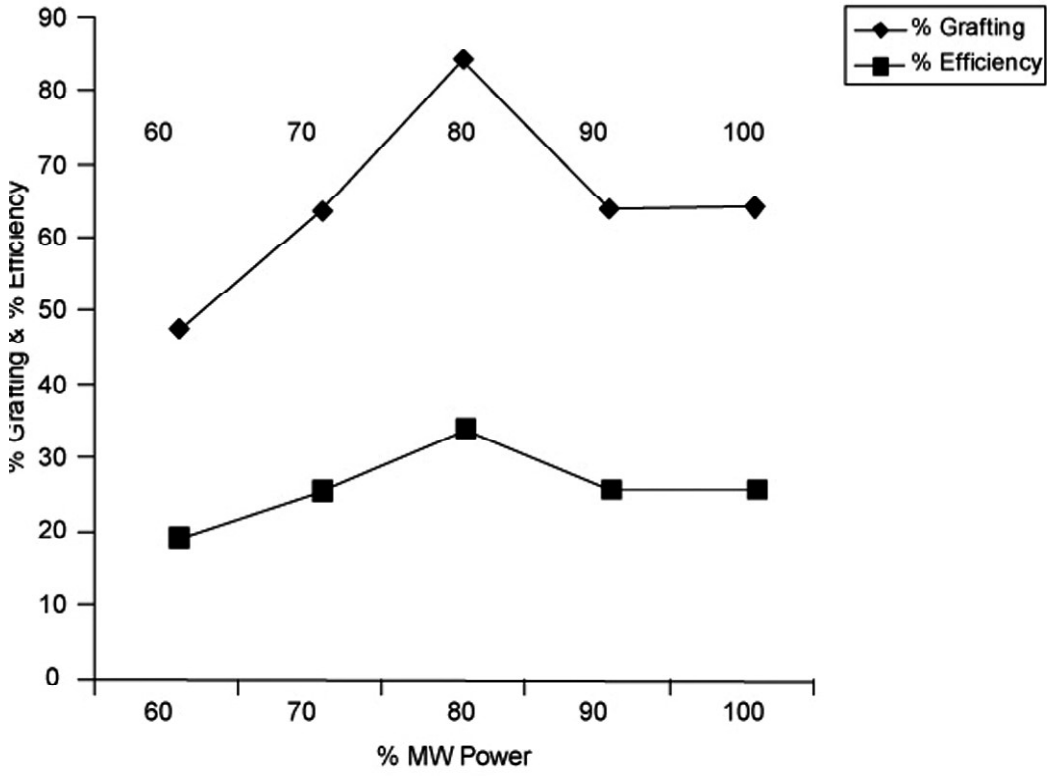


Fig. 2c: Effect of % MW Power on % G and % E {At fixed conc. of seed gum (0.1 g/25ml.), Acrylamide (14 x 10 M/L), total reactior volume 25 ml at 1 Min. exposure time}

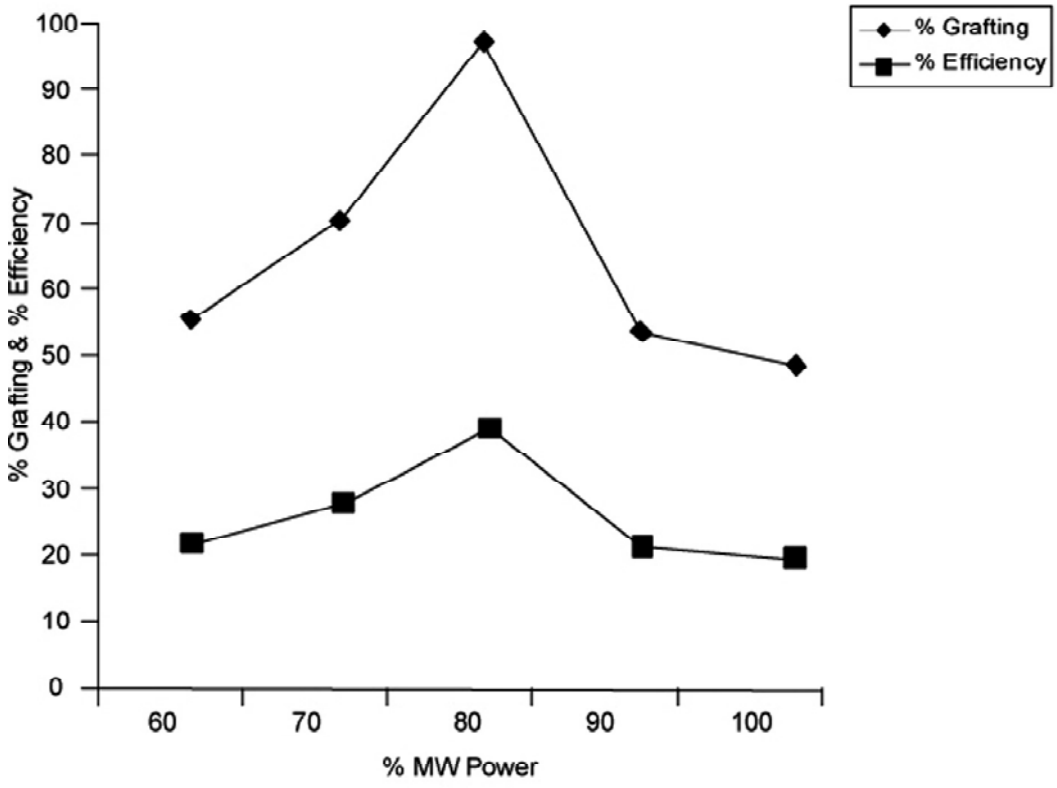


Fig. 2d: Effect of % MW Power on % G and % E {At fixed conc. of seed gum (0.1 g/25ml.), Acrylamide (14 x 10 M/L), total reactior volume 25 ml at 1.5 Min. exposure time}

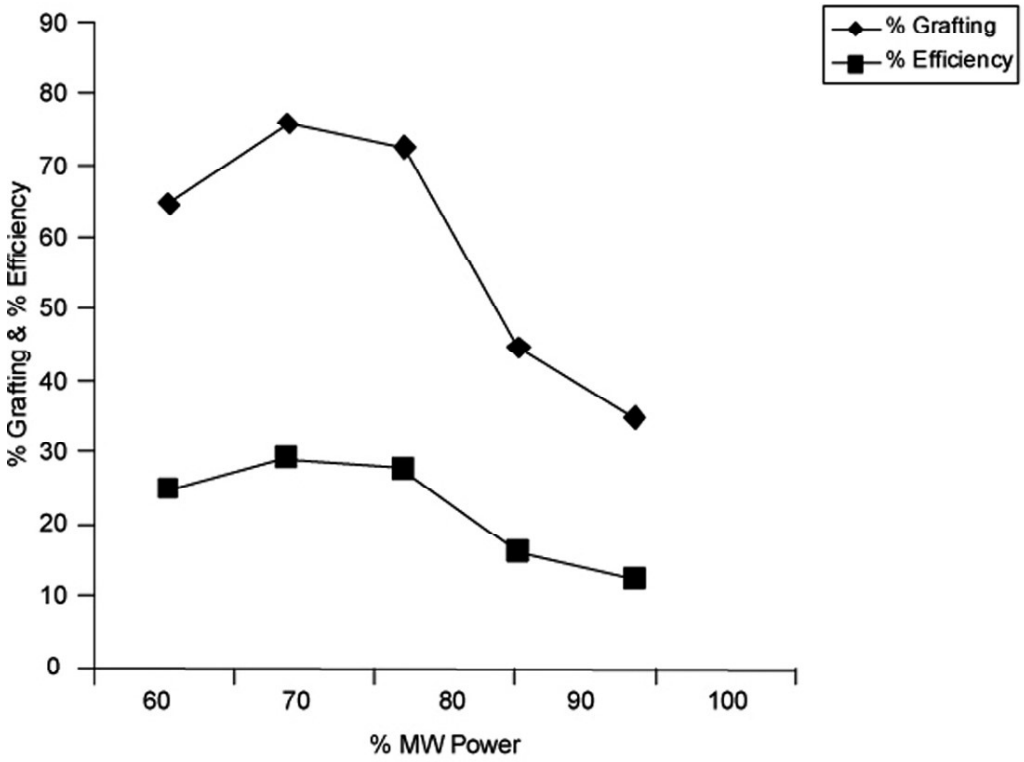


Fig. 2e: Effect of % MW Power on % G and % E {At fixed conc. of seed gum (0.1 g/25ml.), Acrylamide (14 x 10 M/L), total reactior volume 25 ml at 2 Min. exposure time}

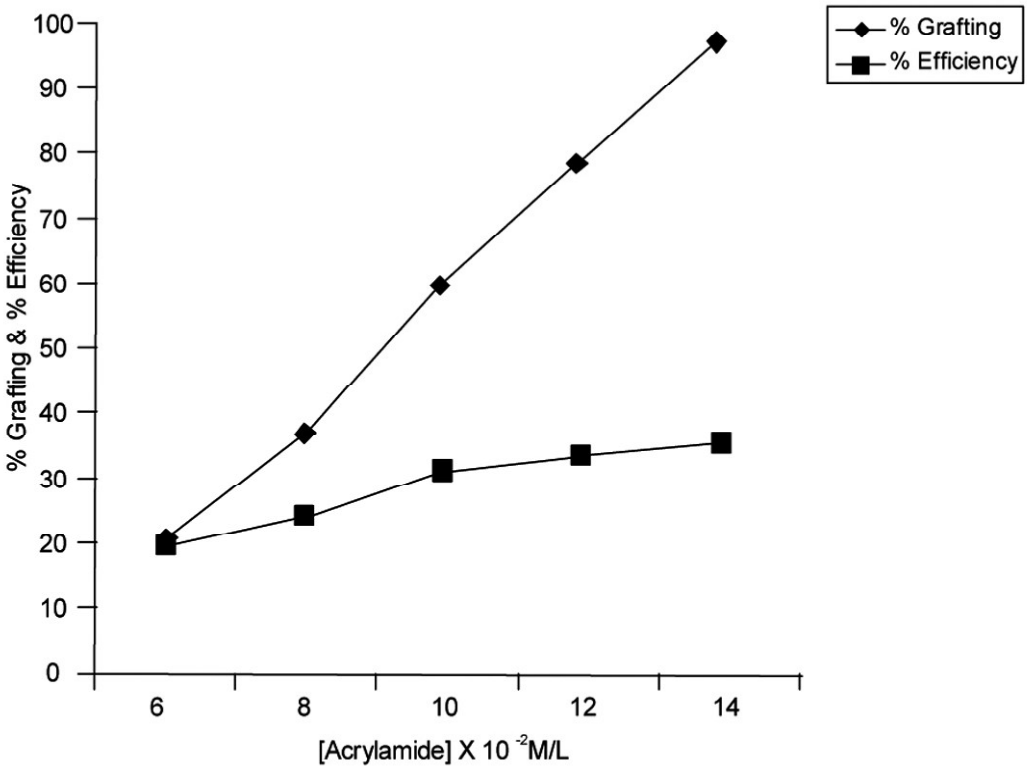


Fig. 3: Effect of acrylamide concentration {At fixed conc. of seed gum (0.1 g/25ml.), total reaction volume 25 ml at 1.5 min exposure time and 80% mW power}

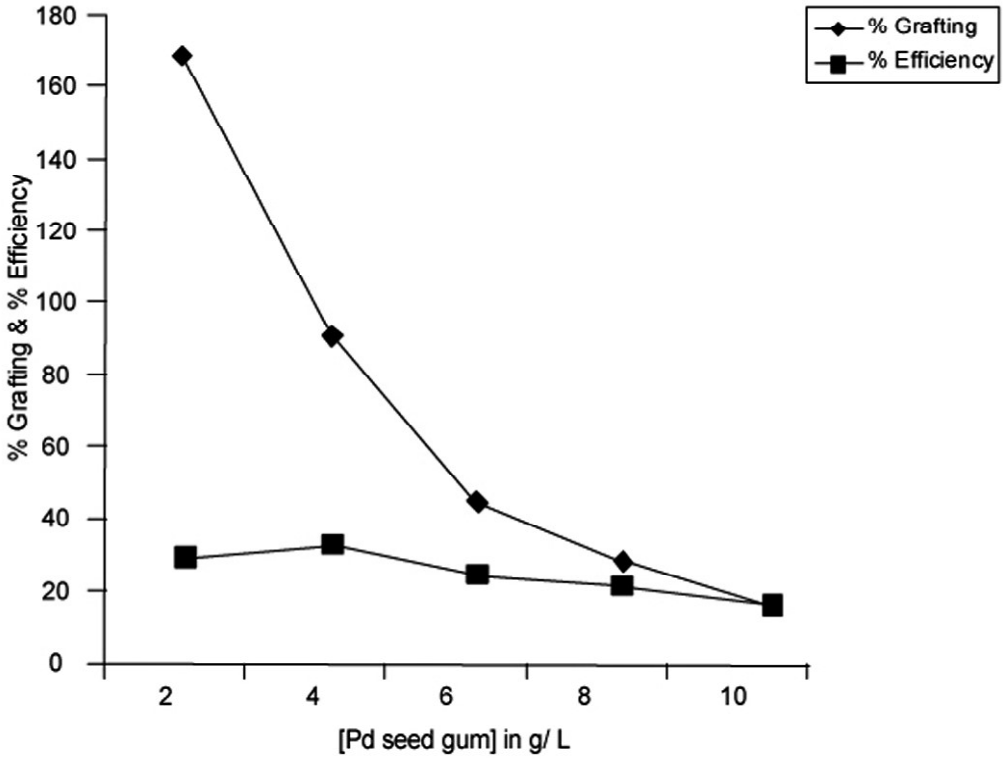


Fig. 4: Effect of *Pithecellobium dulce* seed gum concentration {At fixed conc. of Acrylamide (14 x 10 M/L), total reaction volume 25 ml at 1.5 min exposure time and 80% mW power}

3. Effect of *Pithecellobium dulce* seed gum concentration

The effect of gum concentration (Fig-12) was studied in the range of 2.0-10.0 g/L, keeping other parameters constant. It was observed that both % G and % E decrease with the increase in gum concentration in the studied range, which may be attributed to the increase in the viscosity of the reaction medium, thus hindering the normal graft co-polymerization.

The maximum %E was 38.15%, observed at 80% microwave power in 1.50 min, at a temperature of 100^0C. Thus,the grafting of acrylamide on the PDseed gum under MW irradiation can be done without using any redox system and catalyst. Grafting under MW conditions is compared with conventional thermal grafting in Table-1. Under MW, without a redox system, catalyst yields are almost like conventional thermal grafting (which requires a redox system and catalyst) and reactions are done in a much shorter time.

The possible mechanism for the grafting under MW in the absence of initiators is as follows:

$POH + M \xrightarrow{MW} PO^{\bullet} + M^{\bullet}$

$PO^{\bullet} + M$ '! $POM^{\bullet}$

$POM^{\bullet} + M$ '! $POM_2^{\bullet}$

$POM_2^{\bullet} + M$ '! $POM_3^{\bullet}$

.

$POM_{n-1}^{\bullet} + M$ '! $POM_n^{\bullet}$

$POM_n^{\bullet} + POM_n^{\bullet}$'! (Grafted Polymer)

$M^{\bullet} + M$ '! $M_2^{\bullet}$

$M_2^{\bullet} + M$ '! $M_3^{\bullet}$

$M_{n-1}^{\bullet} + M$ '! $M_n^{\bullet}$

$M_n^{\bullet} + POH$ '! $PO^{\bullet} + M_nH$ (Homo polymer)

POH '! *Pithecellobium dulce* seed gum

M '! acrylamide

MW '! Microwave irradiation

References

1. Bajpai UDN, Jain A, Bajpai AK. Grafting of acrylamide onto Guar gum with the redox system Cu+2/Na2S2O5; *Acta Polymerica*. 1990; **41** : 577.

2. Bajpai UDN, Jain A. Grafting of polyacrylamide onto Guar gum with redox system potassium bromated/thematic acid; *Polymer International.* 1993; 31(1) : 1-7.

3. Bajpai UDN, Rai S. Grafting of acrylamide onto Guar gum using KMnO4/oxalic acid redox system; *J. Appl. Polym. Sci.* 1988; 35 : 1169-1182.

4. Behari K, Taunk K, Tripathi M. Graft co-polymerization of acrylamide on Guar gum using ferrous sulfate-potassium bromate redox couple; *Polymer Preprints.* 1996; 37(2) : 268-269.

5. Behari K, Taunk K, Tripathi M. Cu+2/mandelic acid redox pair initiated graft co-polymerization acrylamide onto Guar gum; *J. Appl. Polym. Sci.* 1999; **71**(5) : 739-745.

6. Behari K, Tripathi M, Taunk K, Kumar Rajesh. Studies of graft co-polymerization of acrylamide onto Guar gum using peroxy diphosphate-metabisulphite redox pair; *Polymer International*. 2000; **49**(2) : 153-157.

7. Boonstra JD, Bekker A. *Ger. Pat.* 1975; 244, 012.

8. Gupta AK, BeMiller JN. A galactomannan form Crotoloria medicine; *Phyto. Chem.* 1990; **29**(3) : 853-858.

9. Hirst EL, Jones JKN. *J. Chem. Soci.* 1948; 1278.

10. Huang M, Chen M. Studies on graft co-polymerization of acrylonitrile and starch under microwave heating*; HuaxueShijie.* 1999; **40**(8) : 426-429.

11. Kapoor VP, Pandey K, Khanna M, Dwivedi AK, Singh S. Pharmaceutical application of galactomannans from the seeds of *Cassia javanica* Linn; In Trends in Carbohydrate Chemistry; Eds., Soni, P.L., Kumar, V., Surya International Publication, Dehradun, India. 1999; **5** : 61-69.

12. Kowkabany GN. Advances in Carbohydrate Chemistry. 1954; **9** : 304.

13. Nayak BR, Singh RP. Development of graft copolymer flocculating agents based on hydroxypropyl guar gum and acrylamide; *J. Appl. Polym. Sci.* 2001; **81**(7) : 1776-1785.

14. Singh Vandana, Tiwari Ashutosh, Tripathi DN, Sanghi R. Grafting of polyacrylonitrile onto Guar gum under microwave irradiation; *J. Appl, Polym.* 2004; **92** : 1569-1575.

15. Singh Vandana, Tiwari Ashutosh, Tripathi DN, Sanghi R. Microwave-assisted synthesis of Guar-g-polyacrylamide; *Carbohydr. Polym.* 2004; **58** : 1-6.

16. Soppinath SK, Kulkarni AR, Aminabhavi TM. Chemically modified Guar gum-g-polyacrylamide based cross-linked anionic microgels as pH-sensitive drug delivery systems: preparation and characterization; *J. Controlled Release.* 2001; **75** : 331-345.

17. Whistler RL. 'Methods in Carbohydrate Chemistry,' Academic Press. 1965; Vol. V, p-332.

18. Xiao X, Zheng Yan-Bing L, Zefang C, Changyi Z. Study of graft co-polymerization onto corn starch by microwave irradiation; *ShiyouHuagong*. 2000; **29**(1) : 19-22.

19. Yanbin L, Xiaoxia Z, Zefang C, Changyi Z. Study of graft co-polymerization of acrylic acid onto starch by microwave irradiation; *HuaxueYanjiu Yu Yingyong*. 1999; **11**(6) : 687-690.

20. Zhenping C, Xiulin Z, Chen G, Xu W, Lu J. Reverse atom transfer radical solution polymerization of methyl methacrylate under pulsed microwave irradiation; *J. Polym., Sci., Polym., Chem. Part-A.* 2002; **40** : 3823-3834.