Persulfate/Ascorbic Acid Initiated Synthesis of Poly(acrylonitrile)-Grafted Tamarind Seed Gum: A Potential Commercial Gum

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ABSTRACT: Acrylonitrile was grafted on to tamarind seed gum using persulfate/ascorbic acid redox initiator and a representative sample of the graft copolymer (Tm-g-PAN) was characterized using infrared spectroscopy (FTIR), X-ray diffraction (XRD) and scanning electron microscopy (SEM). Grafting conditions were optimized where %G and %E were found to increase with the increase in the concentration of the monomer; initiator, and the reaction temperature, whereas increase in gum concentration decreased the %G in the concentration range of 4–12 g/L, The maximum % grafting (%G) and % efficiency (%E) achieved were 305 and 75%, respectively. Water/saline retention, gel forming ability, and the shelf life of the grafted gum solutions were also studied to explore the possibility of its commercial utilization. © 2008 Wiley Periodicals, Inc. J Appl Polym Sci 111: 539–544, 2009

Key words: tamarind gum; poly(acrylonitrile); grafting; persulfate/ascorbic acid redox pair

INTRODUCTION

Tamarind (*Tamarindus indica* L.) is an abundantly[1-6] growing and economically important tree of India. Its fruit pod contains seeds, stringy fibrous material, and an acidic pulp. Polysaccharide from the seed kernels of the tamarind tree is used as industrial gum.[1] Tamarind seed powder,[1] commercially known as TKP, finds extensive use as textile sizer. Creaming and sizing properties of the TKP is due to the polysaccharide present in it, which is galactoxyloglucan[6] where ratio of galactose : xylose : glucose is 1 : 2.25 : 2.8, respectively. Because TKP contains high percentage of proteins and carbohydrates, it is good food for the microorganisms, and therefore, there is great danger that yarn sized with TKP could be attacked. For broader applications, carboxymethylation of tamarind kernel powder was carried out, which not only increased its solubility in cold water but also its stability to microorganism.[7] Ethanolamine derivative[8] of TKP acts as a flocculent-cum-metal ion exchanger and can be used as scavenger for toxic and hazardous metal ions from the effluents of mineral and metallurgical industries.

Besides chemical modifications,[9] vinyl modification of the polysaccharides have also been attempted to obtain the copolymer with improved properties. Recently, tamarind seed mucilage has been grafted with poly(acrylamide)[10] (using Ce (IV) as initiator) and its biodegradation has been investigated. Inclusion of vinylic grafts on polysaccharides[11,12] improves properties as well as susceptibility to the biodegradation. In this study, grafting of acrylonitrile onto the tamarind seed polysaccharide was undertaken for obtaining a copolymer based on tamarind seed polysaccharide and to find out its potential commercial use, the properties of the copolymer were investigated. For the grafting, persulfate/ascorbic acid redox initiator was chosen as this system is reported for excellent grafting of the vinyl monomers on to many seed galactomannans[13] under atmospheric conditions.

EXPERIMENTAL

Ascorbic acid and potassium persulfate (BDH, Analar Grade) were used without further purification. Acrylonitrile (Merck) was distilled in a stream of nitrogen before use. IR spectra were recorded on a Brucker Vector-22 infrared spectrophotometer using KBr pellets. A Brookfield LVDVE viscometer with small sample adapter was used for the viscosity

measurements. X-ray diffraction (XRD) was carried out on an Isodebexlex 2002 X-ray powder diffractometer. SEM analysis was done on EDAX, FEI Quanta 200 machine. For characterization, the copolymer sample having maximum percent grafting was used.

Isolation of the polysaccharide

Tamarind seed flour was extracted[1] with hot water to remove the polysaccharide, which was isolated from the extract by precipitation with 95% ethanol.

Purification of the polysaccharide

To purify[1] the gum, its 2.5% (w/v) solution in water was precipitated with saturated barium hydroxide solution. The complex thus obtained was centrifuged and taken in $1M$ acetic acid, stirred for 8 h, centrifuged and precipitated with 95% ethanol, and subsequently washed with absolute ethanol.

Graft copolymerization

Calculated amount of purified tamarind gum, acrylonitrile and ascorbic acid were taken in water in a 150 mL flask and thermostated at $35 \pm 0.2°C$. After 30 min, a definite amount of persulfate was added, and this time was taken as zero time. Total volume of reaction mixture was kept constant at 25 mL. The Tm-g-PAN was separated from the reaction mixture by precipitating the copolymer with distilled dimethylformamide (DMF).

The percentage and efficiency of grafting were calculated as follows[14]:

$$\% \, Grafting \, (\% \, G) = \frac{W_1 - W_0}{W_0} \times 100 \qquad (1)$$

$$\% \, Efficiency \, (\% \, E) = \frac{W_1 - W_0}{W_2} \times 100 \qquad (2)$$

where, W_1, W_0, and W_2 denote respectively, the weight of the Tm-g-PAN, the original tamarind gum, and the monomer used.

Grafting percent and efficiency were calculated in different sets of the experiment and recorded.

Hydrolysis in aqueous alkali

Tm-g-PAN (2 g on dry basis) was dispersed in 1% NaOH at $100°C$ for 1.5 h. After hydrolysis[14] the sample was precipitated in 600 mL methanol, washed with methanol followed by ethanol, dried and weighed.

Determination of water and saline retention capacity

A weighed amount of dried polymer (0.5 g on dry basis) was taken in a previously dried and weighed sintered glass crucible (G-4) which then was filled with 100 mL of water. After 30 min, suction from a vacuum pump was applied at 700 mmHg and the glass crucible was then weighed to determine the amount of water retained per gram of the dried material, and this was taken as water retention capacity (WRC).[14] Similarly, saline water retention capacity (SWRC) was determined by using 1% aqueous sodium chloride solution.

Gel formation

Gelling property of the gum solution was studied[14] by adding known amount of borax to 2% solution of tamarind polysaccharide.

Viscosity measurement

To prepare the gum solution,[14] a weighed quantity of the gum was dissolved in a minimum required quantity of water by overnight socking, followed by stirring, and then, it was made up to a desired concentration and agitated vigorously for about 15 min till the solution becomes viscous and homogeneous. The measurements were made using a small sample adapter (Spindle No. S-18) of Brookfield LVDVE Viscometer at $30°C$.

RESULTS AND DISCUSSION

Tamarind gum could be very effectively grafted using potassium persulfate/ascorbic acid redox pair under atmospheric conditions. Optimum grafting was obtained at $0.30M$ acrylonitrile, $0.04M$ ascorbic acid, $0.03M$ persulfate, 4g/L gum at $45°C$ where 305% G and 75% E were observed.

Mechanism

Reaction between persulfate and ascorbic acid involves a chain mechanism[15] due to the formation of sulfate ion radicals, which are well-known ion chain carriers. Sulfate ion radical, hydroxyl ion radical, and ascorbate radicals are the primary radicals generated in the redox reactions of persulphate and ascorbic acid. These radicals initiate the vinyl polymerization, as vinyl polymerization is reported to be faster than the H abstraction from the seed gum backbone. The macroradical may be generated by the abstraction of H, from the polysaccharide which may add on to the vinyl monomer generating new radical, and this chain will grow till it combines with other such chains to give a graft copolymer.
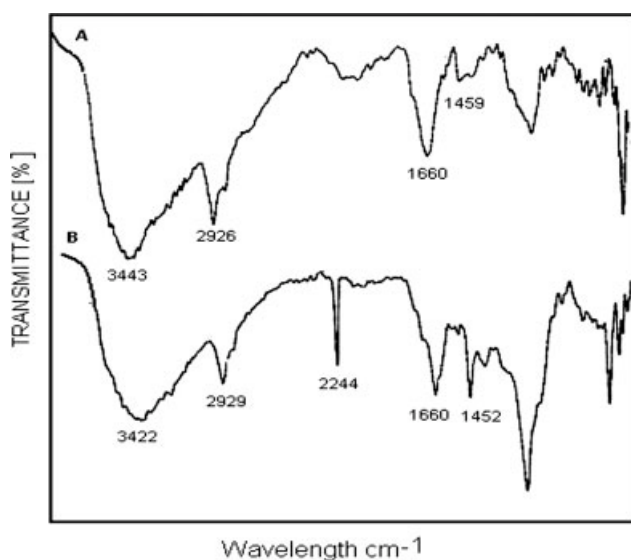
Figure 1 Infra red spectra of (A) Tm gum and (B) Tm-*g*-PAN.

Characterization of the grafted gum

Graft copolymer (Tm-*g*-PAN) was synthesized by grafting acrylonitrile onto the tamarind seed polysaccharide as evidenced by the IR studies. The spectrum of pure tamarind gum has broad strong bands at 3443 cm^{-1} and 2926 cm^{-1} due to O—H and C—H stretching, respectively, whereas IR spectrum of Tm-*g*-PAN has additional strong absorption peaks at 2244 cm^{-1} for —CN stretching and CH$_2$ deformation vibration at 1452 cm^{-1} (Fig. 1). Physical blend of Tm gum and poly(acrylonitrile) after selective removal of poly(acrylonitrile) with DMF showed no absorption in —CN stretching and —CH$_2$ bending region. This substantiates the formation of the graft copolymer.

The XRD pattern of the tamarind gum shows that the gum is amorphous in nature, whereas the Tm-*g*-PAN show sharp crystalline peaks near 2θ 28°−32° due to the presence of poly(acrylonitrile) grafts on to the seed gum backbone (Fig. 2).

A comparison of the scanning electron micrographs of purified Tm and Tm-*g*-PAN (Fig. 3) also confirmed the grafting. The compact, rough and not so homogeneous surface morphology of the tamarind gum seems to have been completely changed after grafting, poly(acrylonitrile) grafts are seen as homogeneous fibrilar depositions at the surface of the tamarind gum.

Optimization of grafting conditions

Grafting conditions were optimized by varying one reaction parameter at the time keeping the others fixed. The results are summarized in Table I.

Monomer variation

The effect of monomer concentration on percent grafting and grafting efficiency was studied in the concentration range of 0.14–0.30 *M* at fixed ascorbic acid (0.025 *M*), persulfate (0.01 *M*), and Tm gum (4 g/L) concentration at 35 ± 0.2°C in 25 mL reaction volume. It was observed that in the studied range, %*G* and %*E* increase with the increase in the monomer concentration; this may be due to the formation of more M_n, generating more grafting sites and also due to the availability of extra monomer for grafting.

Ascorbic acid variation

Effect of ascorbic acid on the grafting was studied in the concentration range of 0.02–0.04 *M* at fixed concentration of acrylonitrile (0.30 *M*), K$_2$S$_2$O$_8$ (0.01 *M*), and tamarind gum (4 g/L) at 35 ± 0.2°C in 25 mL reaction volume. It was observed that with increase in ascorbic acid concentration both %*G* and %*E* increase, which may be due to the formation of more primary free radicals which are capable of propagating the chain.

K$_2$S$_2$O$_8$ variation

Effect of persulfate was studied in the concentration range of 0.010–0.030 *M* at fixed concentration of acrylonitrile (0.30 *M*), ascorbic acid (0.04 *M*), and tamarind gum (4 g/L) in a total reaction volume of 25 mL at 35 ± 0.2°C. The observed increase in %*G* and %*E* with increase in the persulfate concentration may be due to the fact that in the studied concentration range, the activation along the tamarind backbone takes place immediately followed by the grafting of the monomer.
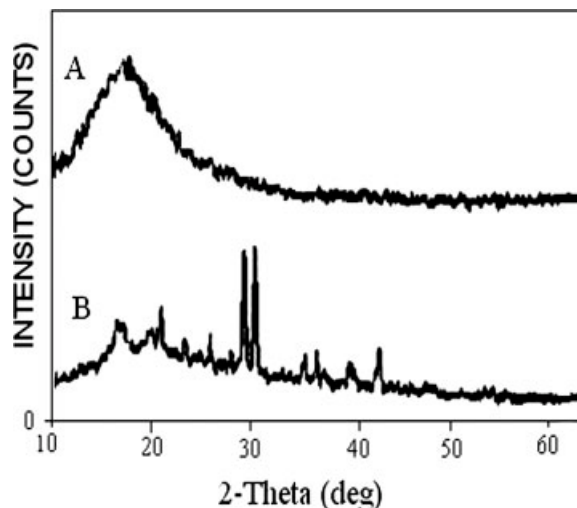
Figure 2 XRD patterns of (A) Tm gum and (B) Tm-*g*-PAN.
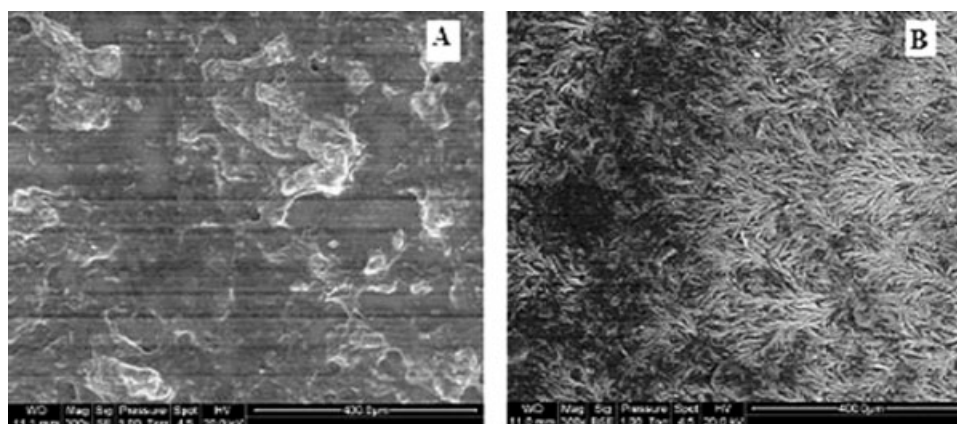
Figure 3 Scanning electron micrographs of (A) Tm gum and (B) Tm-*g*-PAN.

Gum variation

Effect of the tamarind gum concentration on the grafting was studied in the concentration range of 4.0–12 g/L at 0.30 M acrylonitrile, 0.04 M ascorbic acid, 0.030 M $K_2S_2O_8$ in total reaction volume of 25 mL at 35 ± 0.2°C. In the studied range, both %G and %E were found maximum at 4 g/L gum concentration, thereafter the %G and %E decrease which is possibly due to the increase in the viscosity of the reaction medium that causes hindrance to the normal grafting reaction.

Temperature variation

Effect of temperature on grafting was studied in the range of 30–50°C at 0.30M acrylonitrile, 0.04M ascorbic acid, 0.030M $K_2S_2O_8$, and 4g/L Tm gum in a total reaction volume of 25 mL. It was observed that with the increase in the temperature both %G and %E increase. The observed increase in %G and %E may be attributed to the increase in the number of collisions between the monomer and the gum molecules that result due to decrease in the viscosity of the medium at higher temperature.

TABLE I
Optimization of Grafting Conditions by Changing Various Grafting Parameters

S. No.	Temperature in °C ± 0.2°C	Tg (g/L)	AA in (M)	KPS (M)	AN (M)	%G	%E
1	35	4	0.025	0.01	0.14	30	16
					0.18	45	18
					0.22	70	24
					0.26	90	25
					0.30	130	32
2	35	4	0.02	0.01	0.30	80	19
			0.025			130	32
			0.03			142	35
			0.035			165	40
			0.04			190	47
3	35	4	0.04	0.01	0.30	190	47
				0.015		205	50
				0.02		224	55
				0.025		238	59
				0.03		255	63
4	35	4	0.04	0.03	0.30	255	63
		6				230	57
		8				198	49
		10				165	40
		12				135	33
5	30	4	0.04	0.03	0.30	190	47
	35					255	63
	40					280	69
	45					305	75
	50					305	75

Viscosities of Tamarind and Grafted Tamarind Seed Gum at Various Concentrations

S. No.	Gum concentration % (w/v)	rpm	Tm gum		Tg-g-PAN	
			%Torque	Viscosity (cp)	%Torque	Viscosity (cp)
1	0.5	100	21.6	6.75	26.03	19.64
2	1.0	100	19.4	9.60	52.04	25.50
3	1.5	100	12.40	17.60	76.34	37.80
4	2.0	60	10.8	36.43	82.36	42.60
5	2.5	60	9.1	44.50	88.44	76.80
6	3.0	60	8.3	54.00	62.04	84.00

Viscosity

Viscosity of 2% (w/v) solution of Tm and Tm-*graft*-PAN are shown at various concentrations in Table II. For 1% solutions (w/v), the viscosities of Tm and Tm-g-PAN are 9.60 cp and 25.50 cp, respectively. The viscosity of the tamarind gum solution is lost quickly with time due to biodegradation, whereas that of the grafted gum solution remains stable up to 254 h. It was observed that after PAN grafting, viscosity of the tamarind gum increases (due to the increase in the molecular size). Presence of poly (acrylonitrile) grafts in the copolymer is responsible for the higher shelf life of the grafted tamarind gum solutions compared with parent gum (Table III).

Water and saline retention capacity

Water and saline retention capacity decreases after grafting. The water retention property is due to the binding interaction of the hydroxyl groups of the gum through hydrogen bonding with water molecules. The grafting of the vinyl monomers onto the gum occurs through the hydroxyl groups at the seed gum backbone. Thus, grafting decrease the number of the hydroxyl groups and consequently WRC of the grafted gum. Decrease in the water retention is observed to be proportional to the %G (Table III). On hydrolysis with aqueous alkali, the ─CN groups on the grafted chains get hydrolyzed to ─CONH$_2$ and ─COOH groups (which are better water bind-

ing sites) and this increases water binding sites in the saponified Tm-*graft*-PAN and thereby a larger volume of water is bonded (Table IV).

Gel formation

Gelling behavior of the tamarind gum with respect to grafted tamarind gum was studied. It was observed that to gel the graft copolymer solution higher amount of gelling agent was required when compared with native gum solution. Although using the same amount of the gelling agent higher gelling time was required for the grafted gum (Table V). The polysaccharide has numerous cis adjacent hydroxyl groups and therefore with borax it is capable of giving three-dimensional gels. After grafting some of the ─OH groups in the seed gums are replaced with grafted chains leaving fewer cis ─OH groups for the interaction with the gelling agent. Therefore, for gel formation higher concentration of the grafted gum solution or gelling agent is needed.

CONCLUSIONS

Persulfate/ascorbic acid system was for the first time used to effectively graft acrylonitrile on to tamarind seed gum. Using the redox system, the maximum %G and %E achieved were 305% and 75.68% at 0.03M KPS, 0.040M AA, 0.30M AN, and 4 g/L gum in a total reaction volume 25 mL at temperature (45 ± 0.2°C) under atmospheric conditions. The grafting resulted into significant increase in the shelf life of the tamarind gum solutions. The water and

TABLE III
Viscosities of Tg and Tg-g-PAN Gum Solutions with Time

S. No.	Time (h)	Viscosity of Tg	Viscosity of Tg-g-PAN
1	0	36.43	42.60
2	8	32.20	42.60
3	12	27.33	42.60
4	24	19.54	42.60
5	32	11.64	42.60
6	72	4.34	42.60
7	144	2.64	42.60
8	254	2.54	42.60

TABLE IV
Water and Saline Retention Capacities of the Tg, Tg-g-PAN, and Saponified Tg-g-PAN

S. No.	Gum sample	%G	WRC	SWRC
1	Tg-gum	–	8.60	5.45
2	Tg-g-PAN	280	4.25	2.30
3	Tg-g-PAN	305	2.46	1.15
4	STg-g-PAN	280	29.30	–
5	STg-g-PAN	305	36.24	–

TABLE V
Gel Formation of the Tg and Tg-*g*-PAN

Gum	Concentration	Amount of Borax (mg)	Time (s)	Viscosity (cP)
Tg gum	2.0%	50	49	4828
		100	39	7254
		150	27	>10,000
		200	18	>10,000
Tg-*g*-PAN	2.0%	50	–	–
		100	43	8634
		150	24	>10,000
		200	23	>10,000

saline retention capacities and the gelling tendency of the gum were lowered after grafting.

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