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Synthesis, Characterization and Rheological Properties of Guarán Grafted Polyvinylacetate (G-g-PVAc) Copolymer

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ABSTRACT

Guaran was transformed into grafted polymer using polyvinyl acetate monomer. The grafting was initiated through the formation of free radical centers on the polymer backbone by oxidation of guaran with cerium (IV) in nitric acid medium. The degree of grafting was varied by using varying amount of acryl amide vinyl monomer. The rheological properties of the guaran grafted poly vinylacetate copolymer have been studied by varying the degree of grafting, time, concentration, temperature, spindle number and shear rate. Thermal Characteristics of the guaran-grafted polyvinylacetate was studied using thermogravimetric analysis under nitrogen atmosphere. The prepared copolymer was characterized by FTIR.

Keywords: Guarán; hydration time, shear rate, rheological properties; thermogravimetric analysis.

INTRODUCTION

Polysaccharides are recently considered as the subjects for extensive worldwide academic and industrial research. In spite of potential applications of polysaccharides, it is necessary to establish efficient appropriate modifications to explore fully their high potential. A variety of chemical modifications are employed to modify these carbohydrate polymers. The present article provides a comprehensive technique on one of the most promising approaches to modify guarán, i.e., graft copolymerization, with an emphasis on the synthetic aspects.

The polymer grafts of varying degree of hydrophilicity and hydrophobicity can be incorporated into the strongly hydrophilic polysaccharide matrix. A wide range of vinyl monomers with varying degree of hydrophobicity may be grafted on to substrates such as starch [1], cellulose

[2], silk [3], wool [4], rubber [5] and other polymers. Most of the vinyl grafting studies have been carried out on the carbohydrate, starch [6] and cellulose [7]. The Steady of shear and transient properties of starch in dimethylsulphoxide was investigated by Kapoor and M. Bhattacharya [8]. The rheological properties of xyloglucans (XG) from the extra cellular medium of suspension cultured *Nicotiana plumbaginifolia* cells, apple pomace and tamarind seeds, with different structural features and molecular weights, have been studied by Bacis et al [9].

The synthesis and rheological characterization of graft copolymer of Butyl and hydroxymethyl methacrylate on starches was investigated by Gurrauchaga et al. [10]. Zhang and Hu studies of synthesis and thermal degradation of starch graft copolymer [11]. Graft polymerization of (vinyl-alcohol) was investigated by Fanta et al [12]. Mechanical, thermal and rheological properties of methyl methacrylate styrene copolymer were reported by Yongping et al [13]. Preparation and flocculation properties of cationic starch cross linking copolymer have been investigated by You et al [14]. Synthesis of graft copolymer of cellulose with 4-acrylo morpholine and determination of some sorption properties was reported by Temuz et al [15]. Srivastava and Behari studies of synthesis and characterization of Guar-g-N-Vinyl-2-pyrrolidone and investigation of metal ion sorption and swelling behavior [16].

Guaran is a polysaccharide-galactomannan obtained from the seeds of leguminous arid plant *Cymopsis tetragonolobus*. Guaran and its derivatives have been extensively used for a number of applications, particularly oil well drilling, mining, paper, textile, food, cosmetic, pharmaceuticals, agriculture and number of other industries [17]. The viscosity, hydrophilic and hydrophobic nature of the graft, frequency of the grafting and the chain length of graft are of great significance in mineral processing [18] and petroleum industry [19]. The morpholine guaran derivative [20] has been employed for beneficiation of zinc sulphide ore from Rajpura Dariba Mines, Dariba, Udaipur, India. The graft copolymer of guaran were considered to be of special interest, because of the unique structure of guaran matrix, which consists of a long straight chain of mannose residue with a sequence of galactose residue anchored to alternate mannose unit. Thus guaran offers a very regular matrix for synthesis of graft copolymer, incorporating desired physical and chemical properties.

In the present paper, we are reporting our work on grafting of the polysaccharide guaran with polyvinylacetate (PVAc). The new guaran grafted polyacrylamide was synthesized by the new technique of an oxidant-reductant system. In this technique free redial initiates the polymerization of vinyl monomer. This technique preferred over thermal polymerization because they work at low temperature, good field of polymer is obtained, side reaction which occur higher temperature are negligible.

EXPERIMENTAL SECTION

2.1. Chemicals

Analytical grade chemicals supplied by (Loba Chemic, Mumbai) were used in all experiments. Guaran powder was supplied by (Ases Chemical Works, Jodhpur, India). All other compounds used in the synthesis were of commercial high purity grade, and used without further purification

2.2 Preparation of guaran grafted polyvinylacetate (G-g-PVAc):

Guaran solution (0.5%) was prepared by dispersing 5.0 g guaran in 1 liter distilled water in nitrogen atmosphere with constant stirring to avoid lump formation. Ceric ammonium nitrate reagent, 7ml (0.1M in 1M nitric acid) was added with constant stirring at 30⁰C. The stirring was

continued for 30 min. and 8.6g (0.1mole) freshly distilled vinylacetate was added to the reaction mixture. The reaction mixture was stirred for four hour at 30⁰C. The product was recovered by precipitation with equal volume of ethanol and filtered under suction. The products was washed with aqueous ethanol (70, 80, and 90%) and finally with pure ethanol and dried under vacuum. An appreciable amount of guaran was recovered from aqueous filtrate. The guaran-g-PVAc copolymer was purified by extensive solvent extraction by the Tetrahydrofuran for homopolymer PVAc (Polyvinylacetate) coproduced during grafting. The grafted product was a light brown and fluffy powder. The mechanism for the synthesis of guaran-g-PAM copolymer is shown in reaction scheme1.

2.3 Characterization of polystyrene grafted copolymer by IR spectroscopy:

Perkin Elmer IR 983 spectrophotometer was employed to run the spectra using CHCl₃ solvent. In IR spectra, the broad band in the region 3600-3100 cm⁻¹ may be assigned to primary hydroxyl group [21].The range of 2960-2830 cm⁻¹ can be probably be assigned to various stretching frequencies of CH and CH₂ groups . The symmetric and asymmetric stretching modes of CH₂ group vibrate at 2926 cm⁻¹ and 2853 cm⁻¹ respectively. The strong sharp peak at 1750 cm⁻¹ is due to the C=O stretching of carbonyl group.The various bending vibrations of CH₂ groups occur at 720cm⁻¹, 1150cm⁻¹, 1350cm⁻¹ and 1465 cm⁻¹. The IR spectra of guaran grafted polystyrene copolymer is given in fig.2.

2.4 Thermo gravimetric analysis:

For this purpose 951 thermogravimetric analyzer thermobalance was employed. The polymer sample was powdered to the same average mesh size and dried carefully in vacuum desicator. The boat was packed uniformly for analysis. For the dynamic measurement, the system was heated at a constant heating rate of 20⁰C per minute under static air atmosphere till the complete decomposition. The obtained TGA curve is shown in Fig.3. The polystyrene guaran copolymer is found to stable up to 245⁰C and then the degradation was found to be rapid.

2.4 Viscosity measurements:

Viscosity of G-g-PVAc was measured and the effects of different parameters, viz., concentration, temperature, shear rate and spindle size were studied. Measurements were made with Brookfield Synchro-Lectric Viscometer, RVT model, serial no.70156.For all viscosity measurements, a 1.0% aqueous solution of G-g-PVAc was prepared by dissolving 1.0g of G-g-PVAc in 99ml distilled water with vigorous stirring in order to avoid lump formation.

RESULTS AND DISCUSSION

The hydrophilic and hydrophobic character of the G-g-PVAc was found to depend upon the nature of graft, percentage of grafting, and size of graft. It was observed that with the increase in the percentage of hydrophobic graft on the hydrophilic matrix, desired hydrophilic or hydrophobic character can be achieved. Rheological properties characterize the behavior of polymeric systems in deformation and flow of matter. Rheology includes the study of deformation forces as a function of hydration time, temperature, shear rate and certain other parameters. In the Newtonian systems the shearing stress is directly proportional to the rate of shear and viscosity is constant i.e. independent of shear rate. In non Newtonian system viscosity is not constant but is dependent on the shear rate.

The results of variation in viscosities of G-g-PVAc as a function of different parameters are presented in Figure [4-7].

3.1. Effect of hydration time:

It was observed that the rate of hydration of G-g-PVAc studied was considerably lower than the parent polysaccharide. It is known that the parent ungrafted guaran requires about two hours to attain the maximum viscosity. However, in case of grafted products the attaining of the peak viscosity is delayed to the extent of twenty-four hours and thereafter it remains constant as shown in Figure 4, which depends upon percentage and nature of the grafts and the ultimate viscosity was also lower than parent guaran. On drying the graft copolymer, due to flexibility of the polymer chains, the grafts tend to aggregate and in hydration process these aggregates should be loosen by expanding the polymer structure.

It was also observed that with increase in the percentage of vinyl graft the viscosity decreased as shown in Figure 5, which is attributed to the blocking of hydroxyl group in the parent polysaccharide chain by grafted polymer chain.

3.2. Effect of concentration:

An exponential increase in viscosity with increase in concentration was observed as shown in Figure 4 and 5. This behavior is similar to that of the parent polysaccharide. These results are reported in Tables 1, 2 and graphically represented in figures 4, 5.

3.3. Effect of shear rate:

Prabhanjan and Ali [22] studied the shear dependence and pseudoplastic flow behavior characteristics of carboxymethyl and hydroxypropyl derivatives of tamarind kernel powder. The chemical modification decreased the shear dependence of the solution viscosity as the degree of substitution increased. In the case of G-g-PVAc, it was observed that with increase in shear rate, the viscosity also increases as shown in Fig.6 (Table3), which suggests the flow to be non-Newtonian in character. Generally, the water dispersions of hydrocolloids show non-Newtonian flow behavior and undergo shear-thinning. Surprisingly the G-g-PVAc showed shear-thickening. There is however no increase in volume, i.e., dilatancy effect, a phenomenon associated with pastes.

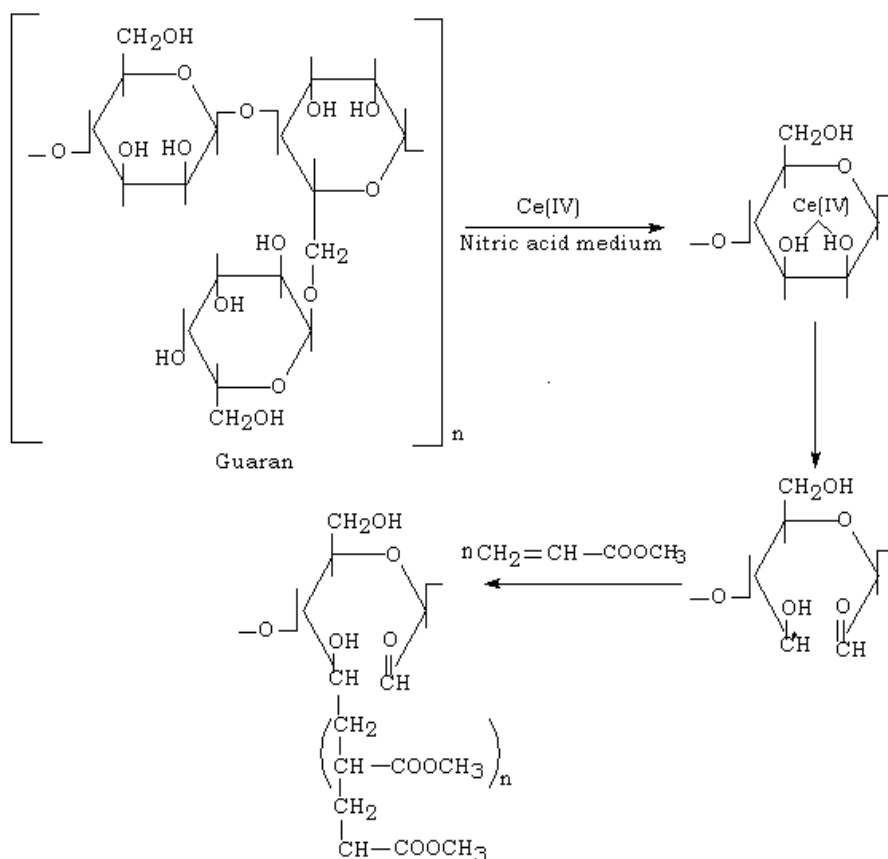
Hence the shear-thickening appears to be due to particle aggregation caused by the interaction between the long chain styrene grafting on the polysaccharide backbone. As the shear rate increases, the transition shifts from low to high concentration solution due to long chain styrene grafting. The interaction of long chain styrene grafting is also strengthened from I.R. spectra as shown in Fig.1.

3.4. Effect of temperature:

The viscosity of G-g-PVAc was found to decrease with the increase in temperature as shown in Fig. 7. This behavior is similar to that of parent polysaccharide. It was also observed that with the increase in the percentage of styrene grafting, the viscosity further decreases due to blocking of hydroxyl group in the parent polysaccharide chain by styrene grafting. . The results are reported in Tables 4, and graphically represented in Fig. 7.

3.5. Effect of different spindles:

A little change in viscosity was observed when measurements were made with different spindles. The constancy of viscosity on changing the spindle establishes the validity and reliability of the measurements.



REACTION SCHEME I : GRAFTING OF VINYL ACETATE ON GUARAN

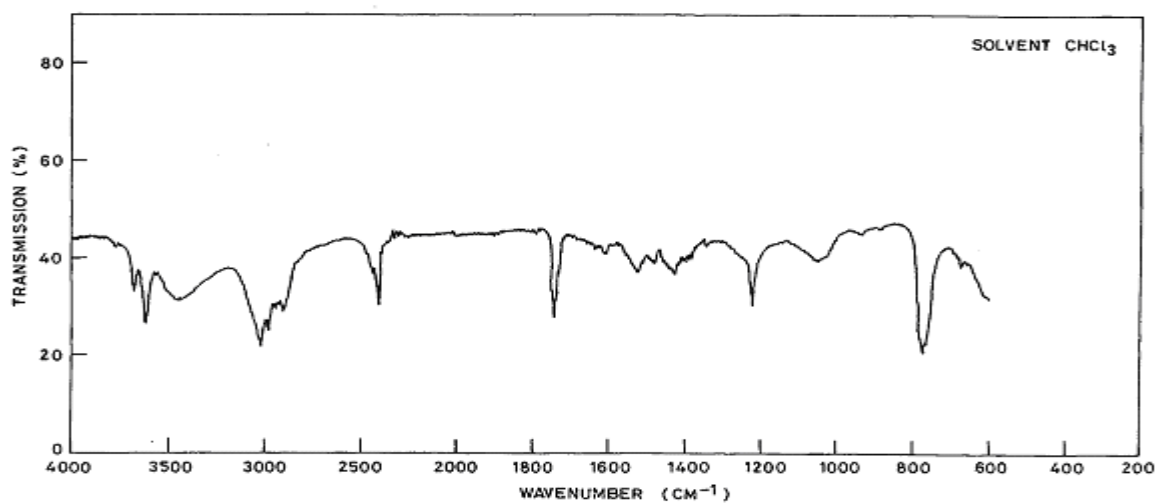


Fig. 2 IR Spectra of guarán grafted polyvinylacetate Copolymer

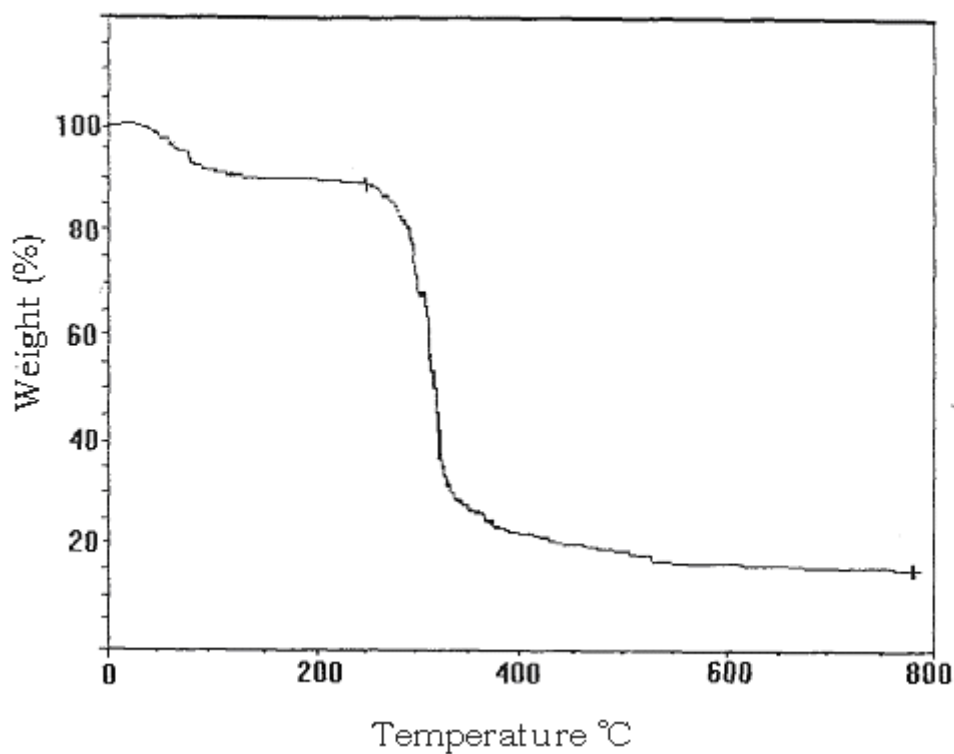


Fig. 3 TGA curve-guaran grafted PVAc copolymer

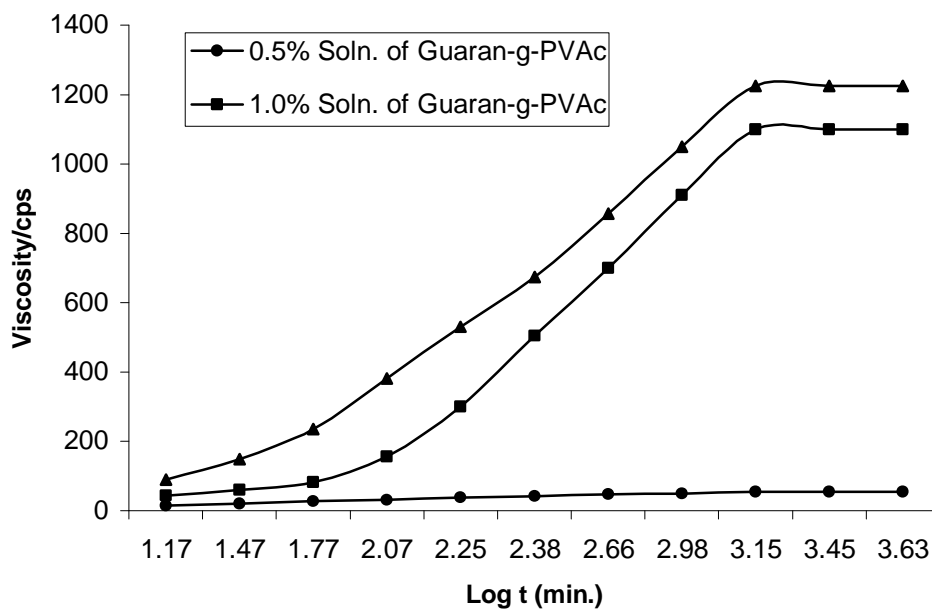


Fig.4. Variation of viscosity with hydration time of G-g-PVAc (D.G.5.21)

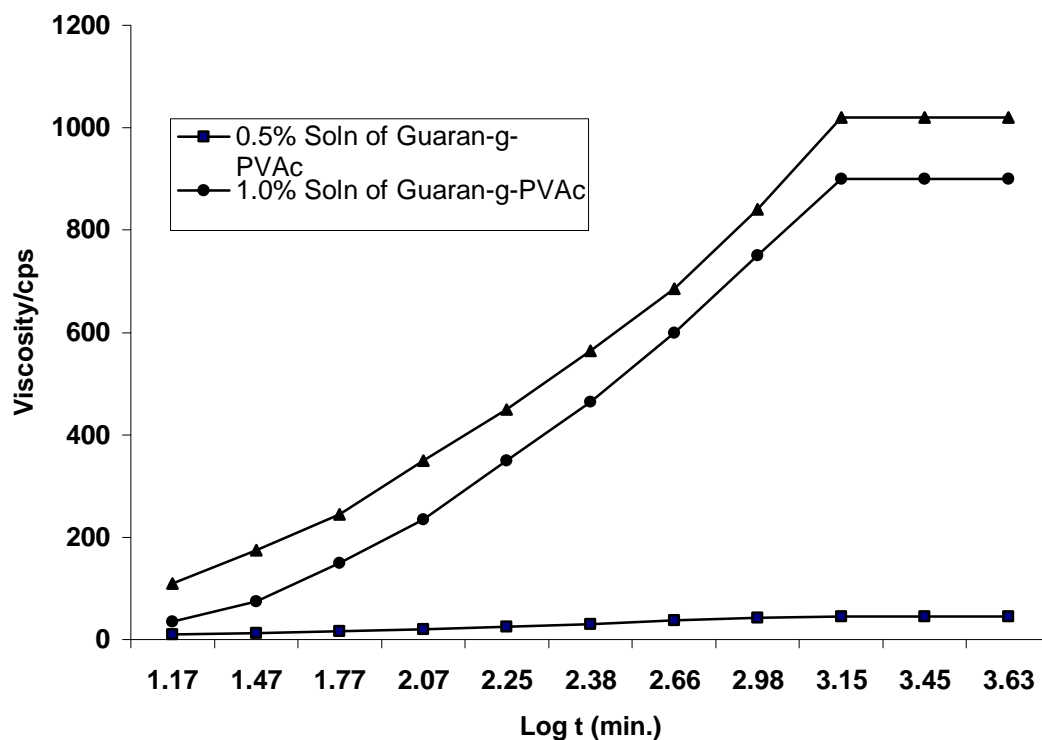


Fig.5. Variation of viscosity with hydration time of G-g-PVAc (D.G 11.0%)

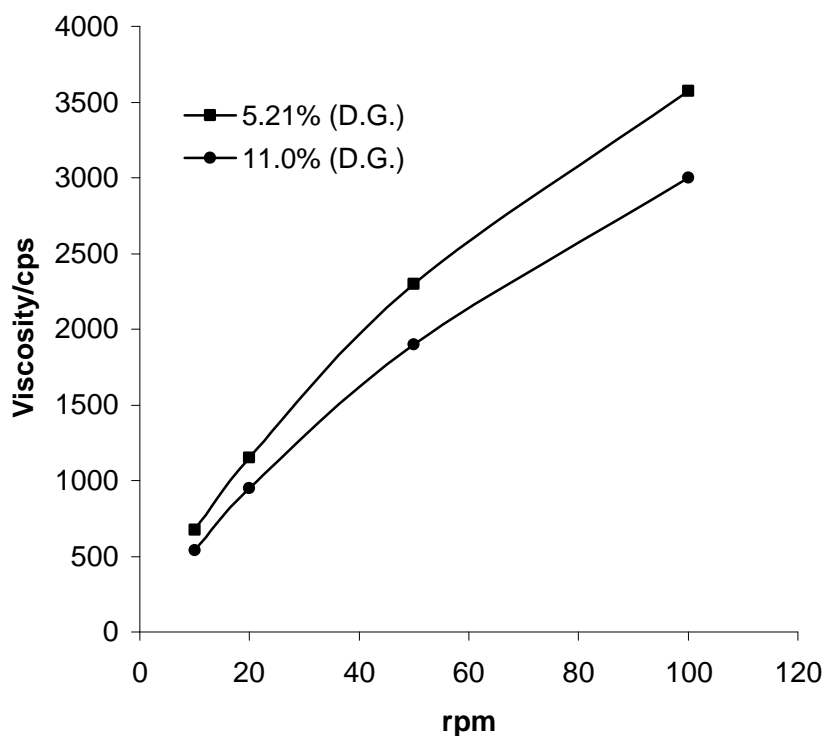


Fig.6. Variation of viscosity of G-g-PVAc with shear

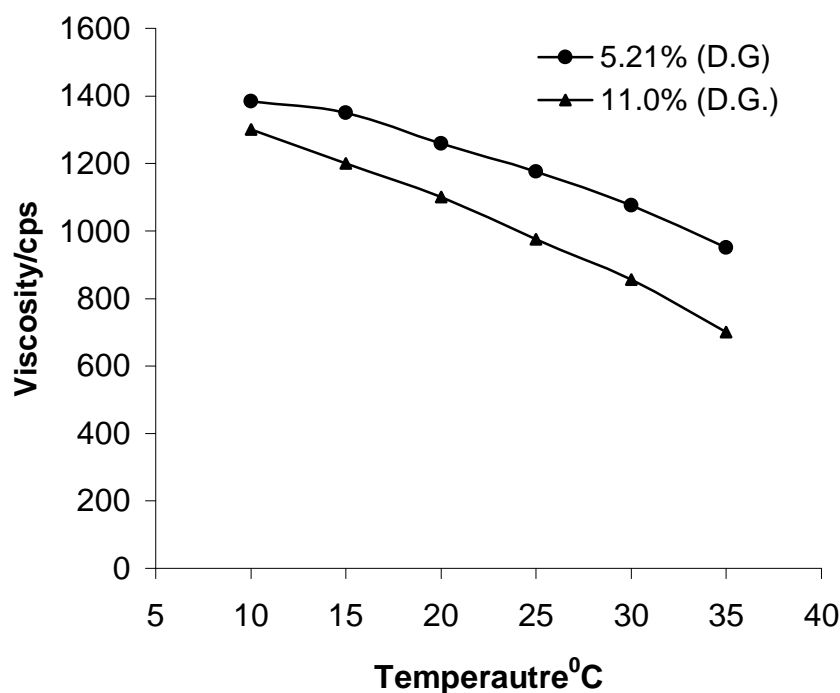


Fig. 7 Variation of Viscosity of G-g-PVAc with Temperature (°C)

Table-1: Variation of viscosity with hydration time of guaran grafted polyvinylacetate (D.G. 5.21%) in aqueous solution of different concentration.

Parameters

Shear rate -20 rpm

Spindle No. 3

Temperature – 25°C

Log t [min]	Solution of Concentration		
Hydration time	Viscosity of Guaran-g-PVAc in Aqueous		
	[0.5%]	[1.0%]	[1.5%]
1.17	15	45	90
1.47	20	60	150
1.77	27	83	235
2.07	32	157	382
2.25	38	300	530
2.38	43	505	675
2.66	47	700	856
2.98	50	910	1050
3.15	55	1100	1225
3.45	55	1100	1225
3.63	55	1100	1225

Table-2: Variation of viscosity with hydration time of guaran grafted polyvinylacetate (D.G. 11.0%) in aqueous solution of different concentration.

Parameters				
Shear rate -20 rpm		Spindle No. 3		Temperature – 25 ⁰ C
Hydration time Log t [min]	Viscosity of guaran-g-PVAc in aqueous solution of concentration			
	0.5%]	[1.0%]	[1.5%]	
1.17	10	35	110	
1.47	12	75	175	
1.77	16	150	245	
2.07	20	235	350	
2.25	25	350	450	
2.38	30	465	565	
2.66	38	600	685	
2.98	42	750	840	
3.15	45	900	1020	
3.45	45	900	1020	
3.63	45	900	1020	

Table-3: Effect of shear rate on viscosity of guaran grafted polyvinylacetate

Parameters			
Shear rate -20 rpm	Spindle No. 3	Temperature – 25 ⁰ C	
Shear rate degree of grafting.	Viscosity (Cps) of Guaran-g-PVAc with different (rpm)		
	[5.21%]	[11.0%]	
10	675	540	
20	1150	950	
50	2300	1900	
100	3575	3000	

Table-4: Effect of viscosity of guaran grafted polyvinylacetate with temperature

Parameters			
Shear rate -20 rpm	Spindle No. 3	Concentration of solution – 1.0%	
Temperature 0 ^o C	Viscosity (Cps) of Guaran-g-PVAc with various degree of Grafting		
	[5.21%]	[11.0%]	
10	1375	1350	
15	1375	1200	

20	1350	1175
25	1150	950
30	1075	825
35	1000	700

CONCLUSIONS

The polyvinylacetate graft copolymer of guaran was considered to be of special interest because of the unique structure of the guaran matrix. The guaran offers a very regular linear matrix suitable for incorporating the desired physical and chemical properties through appropriate grafting and crosslinkage. The viscosity, hydrophilic-hydrophobic nature of the graft, degree of grafting and chain length of the graft are of great significance in mineral processing and petroleum industries [23]

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