SYNTHESIS, CHARACTERIZATION AND RHEOLOGICAL PROPERTIES OF GUARAN GRAFTED POLYSTYRENE (G-G-PS) COPOLYMER

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Abstract
Guaran was transformed into grafted polymer using vinyl monomer. The vinyl monomer used for the graft was styrene. 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 styrene vinyl monomer. The rheological properties of the guaran grafted polystyrene copolymer have been studied by varying the degree of grafting, time, concentration, temperature, spindle number and shear rate. Thermal characteristic of the guaran-grafted polystyrene was studied using thermo gravimetric analysis under nitrogen atmosphere. The prepared G-g-PS copolymer was characterized by FTIR.

Keywords: Grafting, Vinyl monomer, Hydration time, Shear rate, Rheological properties.

INTRODUCTION
Polysaccharides are recently considered as the subject for extensive worldwide academic and industrial research. In spite of potential applications of polysaccharides, it is necessary to establish efficient appropriate modifications to explore their high potential. A variety of chemical modifications are employed to modify these carbohydrate polymers. 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 [6], starch [7] and cellulose [8]. Guar is a polysaccharide-galactomannan obtained from the seeds of leguminous arid plant Cymopsis tetragonolobus. Guaran has now assumed a larger role among the domesticated plants due to its unique functional and rheological properties. Its ability to suspend solid, bind water by hydrogen bonding, control the viscosity of aqueous solution and form strong tough films, have accounted for its rapid growth and used in various industries . Industrial grade guaran is used in, paper, textile processing, explosives, detergents, drilling fluids, ceramics, paints and many other industries [9]. Although it possesses various industrial applications but it’s suffer from some drawback like biodegradability, which limits its application and which can be improved through grafting of vinyl monomer [10, 11]. The studied of rheological properties of the dispersions of starch, guar gum, and their physical mixtures in the different temperature was carried out by Kulkarni et al. [12]. The influence of temperature and salt on viscosity property of guar gum was investigated by Srichamroen [13]. The synthesis and characterization of grafted hydroxypropyl guar gum by ceric ion induced initiation was studied by Nayak and Singh [14]. Grafting of acrylamide on to guar gum with the redox system Cu2+ / Na2S2O5 was investigated by Bajpai 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].

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 [17] and petroleum industry [18]. The morpholine guaran derivative has been employed for beneficiation of zinc sulphide ore from Rajpura Dariba Mines, Dariba, Udaipur, India [19]. The graft copolymer of guaran was 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 polystyrene. The present article provides a comprehensive technique as one of the most promising approach to modify guaran, i.e., graft copolymerization, with an emphasis on the synthetic aspect.

METHODOLOGY
Preparation of Guarana Grafted Polystyrene (g-g-ps) Copolymer

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 minutes and 10.4g (0.1mole) freshly distilled styrene 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 product 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 Guar-g-PS copolymer was purified by extensive solvent extraction with dioxane at 300C.

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for homopolymer PS (Polystyrene) coproduced during grafting. The grafted product was a light brown and fluffy powder. The mechanism for the synthesis of Guar-an-g-PS copolymer is shown in reaction scheme 1.

Characterization of Guar-an graft polystyrene 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. The range of 2960-2830 cm-1 can 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. In aromatic hydrocarbon, a variable C-H stretching absorption occurs in the reign 3050-3000 cm-1, C=C stretching at 1600-1450 cm-1 and bending 900-700 cm-1. The various bending vibrations of –CH2 groups occur at 720cm-1, 1150cm-1, 1350cm-1 and 1465 cm-1. The IR spectra of Guar-an -g-PS copolymer is given in Figure 1.

Thermogravimetric 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 200°C per minute under static air atmosphere till the complete decomposition. The obtained TGA curve is shown in Figure 2. The guaran grafted polystyrene copolymer is found to stable up to 390°C and then the degradation was found to be rapid.

Viscosity Measurements
Viscosity of G-g-PS copolymer 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, 1.0% aqueous solution of G-g-PS was prepared by dissolving 1.0g of G-g-PS 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-PS copolymer 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. The 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-PS copolymer as a function of different parameters are presented in Figure 3 to 6.

Effect of Hydration Time
It was observed that the rate of hydration of G-g-PS copolymer 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 3, 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 4, which is attributed to the blocking of hydroxyl group in the parent polysaccharide chain by grafted polymer chain.

Effect of Concentration
An exponential increase in viscosity with increase in concentration was observed as shown in Figure 3 and 4. This behavior is similar to that of the parent polysaccharide.

Effect of Shear Rate
The flow properties of mixed solution of guar gum and carboxymethyl guar gum, including shear-thinning and viscosity synergism, have been studied by Meng [20]. The chemical modification decreased the shear dependence of the solution viscosity as the degree of substitution increased.

In the case of G-g-PS, it was observed that with increase in shear rate, the viscosity also increases as shown in Figure 5, 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-PS 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 form I.R. spectra as shown in Figure 1.

Effect of Temperature
The viscosity of G-g-PS copolymer was found to decrease with the increase in temperature as shown in Figure 6. This behavior is similar to that of parent polysaccharide. It was also observed that with increase in the percentage of styrene grafting, viscosity further decreases due to blocking of

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hydroxyl group in the parent polysaccharide chain by styrene grafting. The results are shown in Figure 6.

**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.

**CONCLUSIONS**
The Guaran grafted polystyrene copolymer 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 is of great significance in mineral processing and petroleum industries.

*Reaction Scheme I: Grafting of Styrene on Guaran*
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REFERENCES


