

Graft Copolymerization of Acrylic Acid onto Guar Gum

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ABSTRACT: The graft copolymerization of acrylic acid (AA) onto guar gum (GOH) was carried out by a peroxydiphosphate (PDP)–silver(I) system. Grafting ratio, efficiency, add-on, and conversion increase upon increasing the concentration of PDP and acrylic acid, whereas they decrease upon increasing the concentration of guar gum. Upon increasing the concentration of silver and hydrogen ions up to 2.0×10^{-3} and 4.87×10^{-2} mol dm⁻³, respectively, the grafting ratio and efficiency increase but decrease upon further increasing the concentration. The increase in temperature from 30 to 45°C increases the grafting ratio but the conversion efficiency decreases. The optimum time period for graft copolymerization was found to be 2 h. The graft copolymers were characterized by infrared spectroscopy and thermogravimetric analysis. © 2000 John Wiley & Sons, Inc. *J Appl Polym Sci* 77: 39–44, 2000

Key words: graft; copolymerization; acrylic acid; guar gum; PDP-Ag(I)

INTRODUCTION

Guar gum is a naturally occurring carbohydrate polymer. Structurally, it is galactomannan.¹ It enjoys a wide range of usage in industrial applications such as paper, mining, the textile industry, oil wells, etc. Similarly, acrylic acid also possesses some unique characteristics and reactivities, and the polymers derived from it find many commercial applications as a thickener, ion exchange resin, a suspending agent, dispersants, etc.²

Furthermore, different types of starches grafted with polyacrylic acid have wide range of applications in various fields.^{3–8} Prompted by the hitherto unreported graft copolymer viz. guar gum-*g*-polyacrylic acid was prepared by employing a PDP-Ag(I) system. The effect of PDP,

AgNO₃, hydrogen ion, guar gum, acrylic acid concentration, along with time and temperature on grafting parameters has been studied. The graft copolymer has been characterized by IR spectroscopy, and with a view of studying the effect of grafting acrylic acid on thermal stability of guar gum, thermogravimetric analysis was performed.

EXPERIMENTAL

Materials

Acrylic acid and (E. Merck) was distilled over copper turnings under reduced pressure, and a nitrogen stream and the middle fraction was used. Guar gum was procured from Hindustan Gums and Chemicals Ltd. Bhiwani, India, and was used as such. Potassium peroxydiphosphate (FMC, USA) silver nitrate (E. Merck), sulphuric acid (E. Merck), and methanol (E. Merck) were reagent grade, and used as received.

Graft Copolymerization

Guar gum solution was prepared by slow addition of a weighed amount of gum to rapidly stirred

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Table I Effect of [PDP] on Grafting Parameters

[PDP] $\times 10^2$ mol \cdot dm $^{-3}$	% G	% E	% A	% C	% H
1.0	1138.24	84.26	91.92	91.73	15.74
1.6	1179.34	85.43	92.18	93.75	14.57
2.4	1215.33	86.63	92.39	95.27	13.37
3.0	1237.83	87.00	92.52	96.62	13.00

[AgNO₃] = 2.0×10^{-2} mol dm $^{-3}$; [GOH] = 97.8×10^{-2} g dm $^{-3}$; [AA] = 2.0×10^{-2} mol dm $^{-3}$; [H⁺] = 4.87×10^{-2} mol dm $^{-3}$; temp = 35°C time = 120 min.

deaerated triple-distilled water in a reactor. The reaction was carried out under a nitrogen atmosphere at constant temperature. A definitive amount of sulphuric acid, silver nitrate, and acrylic acid was added to the reactor. The reaction was initiated by the addition of PDP. After the specified reaction time the reaction was stopped by letting air into the reactor.

The reaction mixture was poured in a water-methanol mixture where grafted guar gum precipitates out and polyacrylic acid remains in the solution. The precipitate was separated, dried, and weighed. The polyacrylic acid was precipitated by acidifying the filtrate. The polyacrylic acid thus formed as by-product was separated, dried, and weighed.

RESULT AND DISCUSSION

The graft copolymerization was carried out at different concentrations of PDP, silver nitrate, hydrogen ion, guar gum, acrylic acid, as well as for different time periods and temperatures. The graft copolymer thus obtained have been characterized by Fanta's definitions⁹

$$\text{Grafting ratio (\% G)} = \frac{\text{grafted polymer}}{\text{weight of polymer}} \times 100$$

$$\text{Grafting efficiency (\% E)} = \frac{\text{grafted polymer}}{\text{polymer formed}} \times 100$$

$$\text{Add on (\% A)} = \frac{\text{synthetic polymer}}{\text{graft copolymer}} \times 100$$

$$\text{Conversion (\% C)} = \frac{\text{polymer formed}}{\text{monomer charged}} \times 100$$

The amount of homopolymer formed is (100% grafting efficiency).

Effect of PDP

Protonated peroxydiphosphate ions¹⁰ interact with Ag⁺ to form complex (A) that gives free radicals with guar gum [eqs. (1) and (2)]; therefore, as the concentration of PDP increases from 1.0×10^{-2} to 3.0×10^{-2} mol dm $^{-3}$, all the grafting parameters except the homopolymer increase (Table I).

Table II Effect of [Ag⁺] on Grafting Parameter

[AgNO ₃] $\times 10^3$ mol \cdot dm $^{-3}$	% G	% E	% A	% C	% H
1.0	210.50	76.79	67.78	18.61	23.21
2.0	1138.24	84.26	91.92	91.73	15.74
3.0	1107.77	85.71	90.97	79.83	14.23
4.0	739.87	88.09	88.09	57.04	11.91

[PDP] = 1.0×10^{-2} mol dm $^{-3}$; [AA] = 20.0×10^{-2} mol dm $^{-3}$; [GOH] = 97.8×10^{-2} g dm $^{-3}$; [H⁺] = 4.87×10^{-2} mol dm $^{-3}$; temp. = 35°C; time = 120 min.

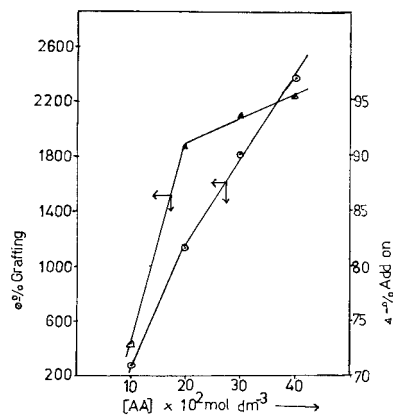


Figure 1 Effect of [AA] on % grafting ratio and % add on: [PDP] = 1.0×10^{-2} mol dm⁻³; [AgNO₃] = 2.0×10^{-3} mol dm⁻³; [GOH] = 97.8×10^{-2} g dm⁻³; [H⁺] = 4.87×10^{-2} mol dm⁻³; temp. = 35°C; time = 120 min.

Effect of AgNO₃

The effect of Ag⁺ on graft copolymerization was studied by varying the concentration of AgNO₃ from 1.0×10^{-3} to 4.0×10^{-3} mol dm⁻³ (Table II). The grafting ratio, add on, and conversion increase upon increasing the concentration of AgNO₃ up to 2.0×10^{-3} mol dm⁻³, but decrease upon further increasing the concentration. The increasing trend in grafting parameters was observed as the concentration of Ag⁺ increases because the concentration of the complex (A) increases [eq. (1)], leading to the increase in the concentration of free radicals. The Ag⁺ acts as a crosslinking agent between two carboxylic groups of the grafted chains. Therefore, as the concentration of Ag⁺ increases, the probability of crosslinking increases; hence, the accessibility of the monomer to the free radical sites decreases; thus, grafting parameters decrease.

Effect of Acrylic Acid

The effect of monomer concentration on grafting reaction was studied at various concentrations of acrylic acid. The grafting ratio, add on, and conversion increase as the acrylic acid concentration is increased from 10.0×10^{-2} to 40.0×10^{-2} mol dm⁻³ (Fig. 1). This is because acrylic acid exhibits Tromdorff's effect, and due to the gelation, the movement of growing polymeric chains is restricted, and hence, the rate of termination is also lowered; therefore, the grafting ratio increases with an increase in acrylic acid concentration.

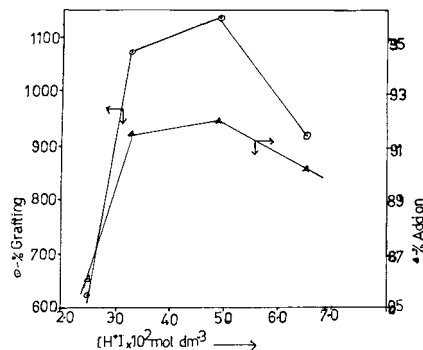


Figure 2 Effect of [H⁺] on % grafting ratio and % add on: [PDP] = 1.0×10^{-2} mol dm⁻³; [AgNO₃] = 2.0×10^{-2} mol dm⁻³; [GOH] = 97.8×10^{-2} g dm⁻³; [AA] = 20.0×10^{-2} mol dm⁻³; time = 120 min; temp. = 35°C.

Effect of Hydrogen Ion

The graft copolymerization conducted at different concentrations of hydrogen ion (Fig. 2). The increase in grafting ratio and efficiency with the increase in the concentration of sulphuric acid to 4.87×10^{-2} mol dm⁻³ is due to the formation of active species¹⁰ H₂P₂O₈²⁻ or H₃P₂O₈⁻, which interacts with Ag⁺ to form a complex that interacts with the guar gum molecule to give free radicals [eq. (2)]. The decrease in the grafting ratio at higher concentrations of hydrogen ion is attributed to the formation of less active species such as H₅P₂O₈⁺² and H₆P₂O₈⁺².

Effect of Guar Gum

The effect of guar gum concentration was studied by varying the concentration of guar gum from

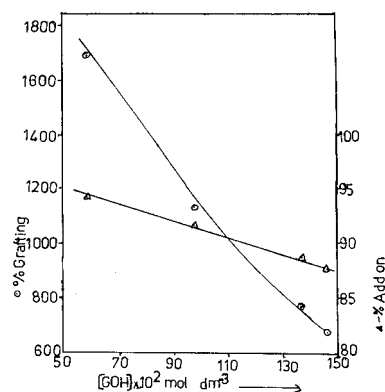


Figure 3 Effect of [GOH] on % grafting ratio and % add on: [PDP] = 1.0×10^{-2} mol dm⁻³; [AgNO₃] = 2.0×10^{-2} mol dm⁻³; [AA] = 20.0×10^{-2} mol dm⁻³; [H⁺] = 4.875×10^{-2} mol dm⁻³; time = 120 min; temp. = 35°C.

Table III Effect of Temperature on Grafting Parameters

Temp. (°C)	% G	% E	% A	% C	% H
30	1117.79	85.63	91.61	88.65	14.37
35	1138.24	84.26	91.92	91.73	15.74
40	1186.09	83.39	92.22	96.58	16.61
45	1206.74	83.22	92.34	98.47	16.78

[PDP] = 1.0×10^{-2} mol dm⁻³; [AgNO₃] = 2.0×10^{-2} g mol dm⁻³; [AA] = 2.0×10^{-2} mol dm⁻³; [GOH] = 97.8×10^{-2} g dm⁻³; [H⁺] = 4.87×10^{-2} mol dm⁻³; time = 120 min.

58.8 to 46.6×10^{-2} g dm⁻³ (Fig. 3). Grafting ratio, add on, and conversion decrease upon increasing the concentration of guar gum. As the concentration of guar gum increases, the viscosity of the medium increases, thereby restricting the accessibility of the monomer to the growing polymeric chain at the active sites leading to the decrease in grafting ratio.

Effect of Temperature

The grafting reaction was carried out at various temperatures ranging from 30 to 45°C (Table III). As the temperature was increased from a 30 to 45°C grafting ratio, add on and conversion increased, whereas efficiency decreased. At higher temperatures it is very likely that PDP might have decomposed, giving rise to free radicals such as PO₄[•], HPO₄[•], etc. These free radicals are capable of abstracting hydrogen ion from guar gum and attacking the monomer molecule to give the respective free radicals. These free radicals interact with each other to give graft copolymer, but with an increase in temperature the collision between monomer free radicals also increased, which led to homopolymerization, thereby decreasing the efficiency.

Effect of Time

The grafting parameters were studied by varying the time period of graft copolymerization from 90 to 180 min (Table IV). The grafting ratio, efficiency, add on, and conversion abruptly increased upon increasing the time period from 90 to 120 min, but upon further increasing the time period a marginal increase in the grafting ratio was observed.

Evidence of Grafting

On comparing the IR spectra of guar gum and guar gum-g-acrylic acid, the following additional bands in the spectra of guar gum-g-acrylic acid were observed: (i) the broad and intense band centered near 3080 cm⁻¹ is attributed to stretching vibration of OH bond; (ii) the observation owing to the carbonyl stretching vibration is shifted to the lower frequency at 1630 cm⁻¹ because of extensive hydrogen bonding; (iii) the bands at 1280 cm⁻¹ and 1450 cm⁻¹ are attributed to C—O stretching and C—O—H bending vibration; and (iv) the band at 940 cm⁻¹ is due to out-of-plane bending of the bonded O—H bond.

The presence of these bands confirm the grafting of acrylic acid onto the guar gum backbone.

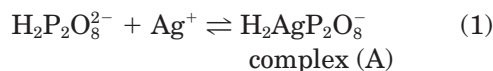
Table IV Effect of Time on Grafting Parameters

Time	% G	% E	% A	% C	% H
90	592.65	70.23	85.53	57.30	29.77
120	1138.24	84.26	91.92	91.73	15.74
150	1146.21	83.53	91.97	92.05	16.65
180	1179.14	82.31	92.18	97.29	19.61

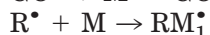
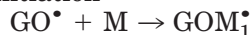
[PDP] = 1.0×10^{-2} mol dm⁻³; [AgNO₃] = 2.0×10^{-3} mol dm⁻³ [AA] = 2.0×10^{-2} mol dm⁻³; [GOH] = 97.8×10^{-2} g dm⁻³ [H⁺] = 4.87×10^{-2} mol dm³; temp. = 35°C.

Mechanism

In a system containing PDP, Ag^+ guar gum, monomer, and hydrogen ion, $\text{P}_2\text{O}_8^{2-}$ interacts with H^+ , giving rise to various protonated species. $\text{H}_2\text{P}_2\text{O}_8^{2-}$, the most active species, forms a complex with Ag^+ , which interacts with the guar gum molecule, giving rise to the guar gum free radical and $\text{HPO}_4^{\bullet-}$ free radical.

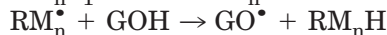


Initiation

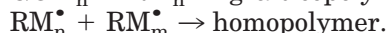
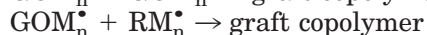
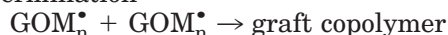


where $\text{R}^\bullet = \text{HPO}_4^{\bullet-}$; M = monomer,

Propogation



Termination



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