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Graft copolymerization of acrylic acid onto guar gum initiated by vanadium (V)–mercaptosuccinic acid redox pair

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Abstract

Guar gum has been modified by graft copolymerization with acrylic acid in aqueous medium using vanadium (V)–mercaptosuccinic acid redox system. The optimum reaction conditions affording maximum grafting ratio, efficiency, add on and conversion have been determined. The grafting parameters have been found to increase with increase in vanadium (V) concentration upto 1.0×10^{-2} mol dm^{-3}, but these parameters decrease on further increasing the vanadium (V) concentration. On increasing the mercaptosuccinic acid concentration from 1.0×10^{-2} to 4.0×10^{-2} mol dm^{-3} grafting ratio, efficiency and add on increase up to 2.0×10^{-2} mol dm^{-3} but decrease with further increase in mercaptosuccinic acid concentration. On varying the acrylic acid concentration from 5.0×10^{-2} to 30.0×10^{-2} mol dm^{-3}, maximum grafting ratio, efficiency and add on have been obtained at 20.0×10^{-2} mol dm^{-3}. The grafting ratio, add on and conversion increase, on increasing the H^+ ion concentration from 1.5×10^{-1} to 6.0×10^{-1} mol dm^{-3}. On increasing the guar gum concentration the grafting parameters increase. The grafting ratio, add on and conversion have been found to increase with time period while efficiency started decreasing after 120 min. It has been observed that $\%G$ increases on increasing the temperature up to 35 °C. The graft copolymer has been characterized by IR spectroscopy and thermogravimetric analysis.

Keywords: Guar gum; Acrylic acid; Graft copolymerization; Mercaptosuccinic acid; Vanadium

1. Introduction

Guar gum is a rigid, non-ionic, neutral carbohydrate polymer. It is one of the few carbohydrate natural polymers (Goldstein, Alter, & Seaman, 1973; Seaman, 1980) which has been used extensively in industry. Utilizing its properties, it has been used in industries such as mining (Atwood & Bourne, 1953), food (Werben, 1950), pharmaceuticals (Eartherton, Platz, & Crosgrove, 1955), and paper, etc. However, Whistler (Whistler, 1973) pointed out the drawback that guar gum suffers from biodegradibility, which limits its applications but this drawback can be improved through grafting of synthetic polymers. It have been reported that the grafting of polyacrylamide onto guar gum gives stability towards biodegradation (Deshmukh & Singh, 1987) and drag-reducing properties can also be enhanced (Deshmukh, Singh, & Chaturvedi, 1985). Acrylic acid, which is a vinyl monomer, possesses some unique characteristics and the polymers derived from it find many commercial applications (Greenwald & Luskin, 1980). Furthermore, grafting of acrylic acid onto different types of natural polymers is reported to have wide range of application in various fields (Chen, Kang, & Neoh, 2000; Hebeish, El-Zairy, El-Rafie, Higazy, & El-sisy, 1991; Pedram, Retuert, & Quijade, 2000). Therefore, an attempt has been made to synthesize guar gum-g-polyacrylic acid.

2. Experimental technique

2.1. Materials

Acrylic acid (E. Merck) was distilled in presence of copper turning under reduced pressure and only the middle

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fraction was used for grafting. Ammonium metavanadate (E. Merck), Mercaptosuccinic acid (Sigma) were used as such. Guar gum was obtained from Hindustan Gums and Chemicals Ltd. as a gift and used as such. Sulphuric acid (E. Merck) was used as source of hydrogen ions.

2.2. Procedure for graft copolymerization

Guar gum solutions were prepared by adding the desired amount to 100 ml triple distilled water in a reactor kept in a thermostat at the desired temperature. A definite amount of mercaptosuccinic acid, acrylic acid, and sulphuric acid solutions were added to the guar gum solution. The stream of nitrogen gas was passed to the solution in the reactor and vanadium (V) solution separately. After the desired time interval, the reaction was initiated by addition of a vanadium (V) solution of the desired concentration. The reaction was allowed to continue for the required time after which the reaction mixture was poured into methanol–water mixture (1:1.4 ratio). The graft copolymer precipitates out, where as polyacrylic acid, remains in the solution. The graft copolymer was separated by filtration and washed with methanol–water mixture two times, so that any homopolymer stuck to the graft copolymer sample passed into the filtrate. The graft copolymer thus obtained was dried and weighed. Polyacrylic acid was precipitated by acidifying the filtrate (Elayaperumal, Balkrishna, & Santappa, 1982) and it was filtered, dried and weighed.

3. Results and discussion

The graft copolymers were characterized according to Fanta's (1973) definition:

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

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

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

$$\text{Efficiency } (\%E) = \frac{\text{Weight of grafted polymer}}{\text{Weight of polymer formed}} \times 100,$$

$$\text{Homopolymer } (\%H) = 100 - \%E.$$

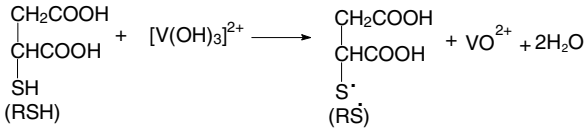
3.1. Effect of vanadium (V) concentration

The effect of vanadium (V) on the grafting parameters was studied by varying the concentration of vanadium ions from 5.0×10^{-3} to 25.0×10^{-3} mol dm^{-3}. The grafting ratio, efficiency, add on and conversion increased on increasing the concentration of vanadium (V) up to 10.0×10^{-3} mol dm^{-3} (Table 1) but decreased thereafter. The increment in the grafting parameters is due to increase in the production of primary free radicals, leading to an increase in the concentration of free radicals, which are responsible for grafting. However, at higher concentration of vanadium (V), oxidative termination of primary free radical leads to decrease in the grafting parameters (Eqs. (1) and (2)):

Table 1
Effect of vanadium (V) concentration

$[V(v)] \times 10^2$ mol dm^{-3}	%G	%E	%A	%C	%H
0.5	102.2	52.7	50.5	13.2	47.3
1.0	125.2	57.4	55.6	14.8	42.6
1.5	110.1	53.1	52.4	14.0	46.9
2.5	81.1	50.0	44.8	11.0	50.0

[Mercaptosuccinic acid] $= 2.0 \times 10^{-2}$ mol dm^{-3}, [acrylic acid] $= 2.0 \times 10^{-1}$ mol dm^{-3}, [guar gum] $= 9.78 \times 10^{-1}$ g dm^{-3}, [H^+] $= 3.0 \times 10^{-1}$ mol dm^{-3}, time = 120 min, temperature = 35 °C.



(1)

$$RS^{\cdot} + V^{5+} \rightarrow \text{Oxidation product} + V^{4+} \quad (2)$$

3.2. Effect of mercaptosuccinic acid

The grafting reactions were conducted by varying the mercaptosuccinic acid concentration from 1.0×10^{-2} to 4.0×10^{-2} mol dm^{-3} (Table 2). It was observed that grafting ratio, efficiency and add on increased as the concentration of mercaptosuccinic acid was increased from 1.0×10^{-2} to 2.0×10^{-2} mol dm^{-3}. On further increasing the concentration these parameters decreased. Initially with an increase in the mercaptosuccinic acid concentration primary free radicals are formed in greater numbers thereby increasing the grafting ratio, efficiency and add on but beyond the cited concentration of mercaptosuccinic acid, the formation of homopolymer increases as evident from the values, and this leads to decrease in the above grafting parameters.

3.3. Effect of acrylic acid

The acrylic acid concentration was varied from 5.0×10^{-2} to 30×10^{-2} mol dm^{-3} (Fig. 1) to study its effects on grafting parameters. The grafting ratio, efficiency and add on were found to increase on increasing the acrylic acid concentration upto 20.0×10^{-2} mol dm^{-3}, but beyond

Table 2
Effect of mercaptosuccinic acid concentration

$[MSA] \times 10^2$ mol dm^{-3}	%G	%E	%A	%C	%H
1.0	112.2	40.6	52.8	18.8	59.4
2.0	125.2	57.4	55.6	14.8	42.6
3.0	92.2	35.0	48.1	18.0	65.0
4.0	77.4	13.1	43.6	20.7	86.9

[V^{+5}] $= 1.0 \times 10^{-2}$ mol dm^{-3}, [acrylic acid] $= 2.0 \times 10^{-1}$ mol dm^{-3}, [H^+] $= 3.0 \times 10^{-1}$ mol dm^{-3}, [guar gum] $= 9.78 \times 10^{-1}$ g dm^{-3}, time = 120 min, temperature = 35 °C.