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Microwave assisted synthesis of guar gum grafted sodium acrylate/cloisite superabsorbent nanocomposites: Reaction parameters and swelling characteristics

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ABSTRACT

In this study, superabsorbent nanocomposites of guar gum grafted sodium acrylate have been synthesized via both microwave and conventional techniques. The reaction parameters of both techniques were optimized and the microwave assisted method was proved to have higher grafting yield with lesser time of reaction as compared to the conventional method. X-ray diffraction and scanning electron microscopy analyses revealed that cloisite was exfoliated and uniformly dispersed in guar gum grafted sodium acrylate matrix. The results show that introducing cloisite into the guar gum grafted sodium acrylate network improved the swelling capability and the swelling rate of the superabsorbent nanocomposite was found to be enhanced at an optimal loading of 10% cloisite. The nanocomposites showed high water absorbency within a wide pH range. Preliminary studies on crystal violet dye removal showed promising results.

1. Introduction

Superabsorbents are hydrophilic polymers with the ability to absorb, swell and retain large quantities of aqueous liquids even under some pressure. Conventional superabsorbents in practice are mainly expensive petroleum based synthetic polymers and their usage may cause serious environmental impacts [1]. Hence the development of low cost and biodegradable superabsorbents derived from natural polymer using eco-friendly additives are of greater interest due to their environmental and commercial advantages. The unique properties of biobased superabsorbent hydrogels have found potential application in many fields such as agriculture [2–4], hygiene products [5], wastewater treatment [6,7] and drug delivery systems [8]. Polysaccharides such as starch [9], chitosan [10], cellulose [11], gelatin, alginate [12] and many kinds of gum have been utilized for fabricating eco-friendly hydrogels using grafting method. Even though, the desired chemical and physical properties of polysaccharide based copolymeric materials are obtained using conventional grafting, it may also lead to polysaccharide backbone degradation and are not amenable to block formation of undesired homopolymer, lowering the copolymer yield and posing problems in the commercialization of the grafting procedures. The requirement for an inert atmosphere is an added disadvantage for many conventional grafting procedures [13]. Unlike conventional grafting, the microwave irradiation grafting technique significantly reduces the use of toxic solvents, apart from reduced reaction times from hours to minutes to even seconds ensuring high yields [14,15] along with synthesis via microwave technique is product selectivity. Hence, a cleaner and greener approach is suitable for commercial mass production. Moreover, in many instances, microwave synthesized polysaccharide copolymers exhibit better properties for commercial exploitation. The extent of physico-chemical stresses to which the materials are exposed during the conventional techniques is also considerably reduced than their conventionally synthesized counterparts [13]. Guar gum (GG), as a representative natural vegetable gum, is a branched biopolymer with β-D-mannopyranosyl units linked with single-membered α-D-galactopyranosyl units occurring as side branches. Many researchers have carried out studies on grafting GG with monomers like acrylamide, acrylonitrile and ethylacrylate [13]. In the design and development of new superabsorbent hydrogels, high swelling capacity, fast swelling rate and good gel strength are especially desired. In recent days polymer/clay nanocomposites have received intense research interest driven by the unique properties which can never be obtained by

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micro-size fillers or especially by other nanofillers. By incorporation of inorganic layered silicates into pure polymeric networks with uniform dispersion not only reduce the production cost, but can also improve the water-absorbing properties and the gel strength of the resultant absorbing materials [15]. Studies on swelling kinetics in guar gum-g-poly (sodium acrylate)/rectorite [7], superabsorbent nanocomposite revealed improved performance and swelling kinetics. However, studies on grafted guar gum superabsorbent nanocomposites are very few. Hence in the present study, sodium acrylate (Na Acry) has been grafted to guar gum via conventional and microwave irradiation techniques. The optimization of the reaction parameters both for conventional and microwave grafting techniques were performed and compared. The optimized microwave conditions were then used to synthesize a series of – guar gum grafted sodium acrylate/cloisite superabsorbent nanocomposites with varied loading of cloisite. The swelling characteristics of these nanocomposites have been examined in different mediums. A preliminary study on the adsorption of crystal violet cationic dye has been carried out using these superabsorbent nanocomposites.

2. Experimental

2.1. Materials

Sodium acrylate was purchased from Sigma Aldrich (USA), Organically modified clay (Cloisite 30B) was purchased from J.K. Impex, Mumbai, Guar gum with molecular weight 4.22×10^6 [16], ammoniumpersulphate (APS), N,N′-methylenebisacrylamide (MBA), crystal violet dye and acetone of analytical grade were procured from S.d. Fine chemicals, Mumbai, India.

2.2. Grafting of guar gum by conventional method

GG (1.00 g) was dissolved in 100 mL distilled water in a 250 mL beaker equipped with a mechanical stirrer, a thermometer and a nitrogen line. 2 g of sodium acrylate was then added to the dispersion and kept for few minutes to form colloidal slurry. Then, 4 mL of the aqueous solution of the initiator APS (100 mg) and cross linker MBA (95 mg) was added to the reaction flask under continuous stirring and kept at 70 °C for 1 h. A nitrogen atmosphere was maintained throughout the reaction period. After the completion of polymerization the solution is washed with acetone to dissolve the undesired products and precipitate the copolymer. The obtained gel products were dried to a constant mass and grounded into a fine powder using pestle and mortar. The grafting yield or percentage grafting (G) was calculated using the equation below.

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

where W_0 and W_1 denote the weight of GG and graft copolymer, respectively.

2.3. Grafting of guar gum by microwave method

GG (1.00 g) was dissolved in 100 mL distilled water in a 250 mL beaker equipped with a mechanical stirrer and a thermometer. To the solution, 2 g of sodium acrylate was added and kept for few minutes to form colloidal slurry. Then, 4 mL of the aqueous solution of the initiator APS (100 mg) and cross linker MBA (95 mg) was added to the reaction flask under continuous stirring and kept till a homogenous mixture is obtained. The solution is kept in the microwave reactor with 800 W and the temperature set to 70 °C for different timings. After the completion of reaction time the solution is washed with acetone to dissolve the unreacted product and precipitate the copolymer. The obtained gel products were dried to a constant mass and ground to fine powder using pestle and mortar. The grafting yield or % graft was calculated using Eq. (1).

2.4. Grafting of cloisite with sodium acrylate

To 1% (w/v) solution of guar gum in distilled water, a measured quantity of cloisite was added and sonicated for 30 min to ensure homogenous dispersion. To this mixture the optimized concentrations of monomer, initiator and cross linker was added. The reaction was carried out as per the previous microwave grafting procedure but with the optimized time. The grafting yield or % graft was calculated using the Eq. (1).

3. Characterization

3.1. Fourier transform infrared spectroscopy

The Fourier transform infrared spectroscopy (FTIR) analysis of pure guar gum, pure cloisite, guar gum grafted sodium acrylate and cloisite grafted sodium acrylate were carried out using FTIR spectrophotometer (model: Perkin-Elmer spectrum 1000) between 300 and 4000 cm^{-1}.

3.2. X-ray diffraction studies

X-ray diffraction (XRD) measurements for the composites have been performed using advanced diffractometer (PANalytical, XPERT-PRO) equipped with Cu Kα radiation source (X = 0.154 mm). The diffraction data were collected in the range of $2\theta = 3–60^\circ$ using a fixed time mode with a step interval of 0.05°.

3.3. Thermo gravimetric analysis (TGA)

The TGA of guar gum and grafted sodium acrylate nanocomposites were carried out by using Perkin-Elmer Pyris Diamond 6000 analyser in an atmosphere of nitrogen (Perkin Elmer Inc., Shelten, (T)). The sample was subjected to a heating rate of 10 °C/min in a heating range of 20–900 °C.

3.4. Scanning electron microscope (SEM)

The morphological characterization of the specimens was carried out using a scanning electron microscope (SEM) (JOEL, JSM-840 A microscope). The specimens were gold sputtered prior to microscopy.

3.5. Transmission electron microscopy

Transmission electron microscopy (TEM) for nanocomposites has been performed using a JOEL, Model 782, operating at 200 kV. TEM specimens were prepared by dispersing the composite powders in methanol by ultrasonicating. A drop of the suspension was put on a TEM support grid (300 mesh copper grid coated with carbon). After drying in air, the composite powder remained attached to the grid and was viewed under the transmission electron microscope.

3.6. Measurement of equilibrium water absorbency and swelling in different buffer mediums

The equilibrium water absorbency and swelling has been carried out by the tea bag method [17]. A 0.05 g of sample was immersed in distilled water for 4 h to reach swelling equilibrium. The swollen gels were filtered out and then drained. After weighing the swollen