

Studies and Characterizations: Effective crosslinking agent on Guar gum –Poly(acrylamide) hydrogel

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Abstract

Guar gum and polyacrylamide crosslinked hydrogel has been made in aqueous medium. Polymerization of acrylamide has been achieved in the presence of guar gum using potassium persulphate as initiator. Guar gum-Polyacrylamide hydrogel prepared with N, N'-methylene-bis-acrylamide (MBA) as the crosslinking agent. The effect of using crosslinking agents on the gel structure has been evaluated by studying the swelling behavior of gels made with different amounts of crosslinking agents. Swelling studies indicate as the optimum concentration of MBA for obtaining maximum swelling. The gels have been characterized by FTIR, elemental analysis, SEM, DSC and TGA techniques.

Key words: Guar Gum, polyacrylamide, crosslinker, Elemental analysis,

1.Introduction

Hydrogels that exhibit swelling changes in response to environmental changes such as temperature, pH, electrical field, radiation, etc. are promising as intelligent materials. They attract increasing interest in various biomedical, industrial and agricultural applications [1-5]. The swelling characteristics of the gel are of utmost importance in most of these applications which can be greatly controlled by the chemical structure of the gels. [6, 7].

Guar gum(Gg) is a high molecular weight hydrocolloidal hetero-polysaccharide composed of galactan and mannan units. Guar gum has been modified by derivatization, grafting and network formation to improve its property profile for a wide spectrum of end-uses. Using different initiating systems grafting of acrylonitrile[8], acrylic acid [9] and acrylamide [7] onto guar gum has been reported.

Polyacrylamide (PAAm) is a water-soluble polymer with a hydrophobic main chain and a hydrophilic side group. Polyacrylamide is a well known hydrogel, and polyacrylamide, by

carrying out polymerization of acrylamide in the presence of guar gum in aqueous medium using KPS as initiator and crosslinking agent, MBA. The effect of the nature and concentration of the crosslinking agents on swelling behavior of the gels has been evaluated.

2. Materials and Methods

2.1 Materials

Acrylamide(AAm), N,N'methylene-bis-acrylamide(MBA) were obtained from s.d.Fine chemicals, Mumbai, India. Guar gum(Gg), potassium persulfate(KPS) were obtained from Merck chemical, All other reagents were of analytical grade. Distilled water was used in the preparation of hydrogels and for swelling studies.

2.2. Synthesis of Guar gum-Poly(acrylamide)[Gg-PAAm] hydrogel

Hydrogels were prepared by Acrylamide (AAm) and Guar gum (Gg) by free radical polymerization. Briefly, 0.2g of GG was dispersed in 5mL water and stirred 5hr. 0.1g AAm and 0.0125g KPS dissolved in 2.5mL water was added to the Gg solution and mixed well. 0.002g of MBA dissolved in 2mL water, added to above solution and mixed well, was carried out at 60⁰C for 2hrs. Crosslink hydrogel was purified by soxhlet extraction to remove unreacted materials in the reaction. The hydrogel were dried at 50⁰C under vacuum (60mm Hg) overnight. Same procedure was followed by synthesis of various MBA concentrations like 0.006(0.38 mol), 0.008(0.5 mol), 0.013(0.8 mol) & 0.020(1.2 mol)g & naming by Gg-PAAm-1, Gg-PAAm-02, GG-PAAm-03 & Gg-PAAm-04 respectively.

2.3. Characterization

2.3.1. FTIR spectroscopy

The samples Gg & Gg-PAAm-02 were subjected to FTIR spectroscopy in a Fourier transform infrared spectrophotometer (Perkin-Elmer, USA) in range of (4000–400 cm⁻¹) as KBr pellet.

2.3.2. Scanning Electron Microscopic (SEM)

The SEM analysis of Gg & Gg-PAAm-02 crosslinked hydrogels were carried out with a JEOL-JSM 5800LV scanning electron microscope. The micrographs were recorded with magnification of 1000 and 500 under voltage of 20kV.

2.3.3. Thermal Analysis

2.3.3.1 TGA studies

The thermogravimetric analysis (TGA) of Gg and GG-PAAm-02 samples was carried out with TGA instrument (Model: SDT Q600 V20.9, Japan). The study was performed up to 700 °C, in inert atmosphere (of nitrogen). The heat ingrate was uniform in all cases at 5 °C/min.

2.3.4. Elemental Analysis

Elemental analyses of Gg, AAm, GG-PAAm-02, samples were carried out on a Vario EL III CHN analyzer (Germany) and percentages of carbon, hydrogen, and nitrogen were determined.

2.4. Swelling studies

The swelling behavior of the hydrogels under different pH conditions was investigated by carrying out swelling measurements in aqueous buffer media of pH-1.2, 6.7 and 9.0 using standard buffer solutions, at 30 °C. The weight measurements with time were made using an electronic balance (Shimadza AUX120, Japan) with an accuracy of ±0.1mg. Pre-weighed dry hydrogels were immersed in excess of the buffer solution, maintained at predetermined temperature. After specific intervals of the time, the gels were removed from the medium. The surface adhered liquid drops were wiped with blotting paper and the increase in weight was measured. The measurement was continued till the weight of the swollen gels attained constant values. The swelling ratio, ‘%SR’ of the gel was calculated using the following expression,

$$\% \text{Swelling Ratio} = \frac{\text{Weight of swollen gel} - \text{Weight of dry gel}}{\text{Weight of dry gel}} \times 100$$

3.0: Result & Discussion:

3.1. FTIR

The FTIR spectra of Gg & GG-PAAm-02 samples have been compared in Fig. 1. In the spectra of GG-PAAm-02 network (Fig.1b), the broad peak that appeared at 3217.2cm⁻¹ is due to O–H stretching and other important peaks observed at 1156.5, 1093.9, 1020.2cm⁻¹ are attributed to C–O–C stretching from glycosidic linkages and O–H bending of GG component. In addition, the FTIR spectrum of GG-PAAm-02 gel shows peaks corresponding to amide groups. The N-H stretching appears as a shoulder band around 3400cm⁻¹ and has overlapped with a broad peak between 3500 to 3200 cm⁻¹ of the hydroxyl group. Further, the broadness of the O-H peak of GG (Fig. 1a) has been reduced in GG-PAAm-02 due to the reduction in the number of O-H groups on account of their involvement in grafting and crosslinking

reactions. The peaks which appear at 2854 and 1461.5 cm^{-1} are attributed to amide C-H stretching and bending respectively.

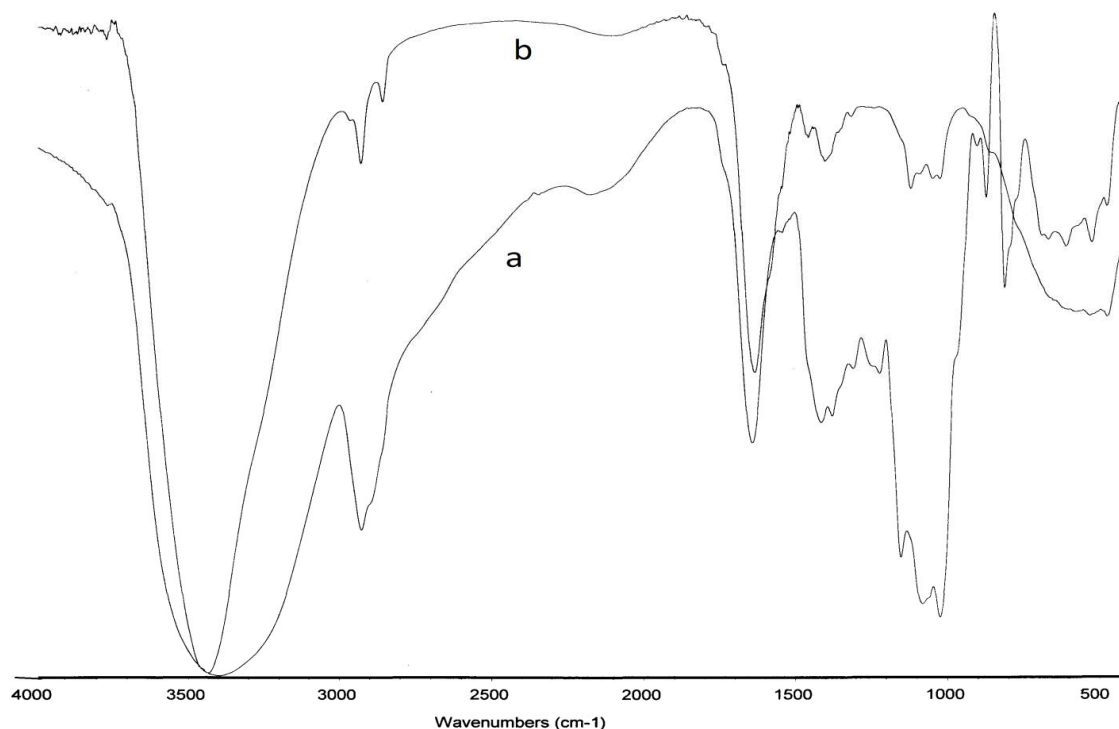


Fig. 1. FTIR characterization of Gg (a) & GG-PAAm-02 (b)

3.2. Thermal Analysis:

Differential Scanning Calorimetry (DSC) Analysis:

In the DSC of Gg (Fig.2a), the broad endothermic peak in the range 50-120°C arises due to due to loss of absorbed water and the other smaller endothermic peak around 320-355°C is due to degradation of polymer backbone. In Gg-PAAm-02 (Fig.2b) network, the endothermic arising due to loss of water appears at 50-100°C with considerable reduction in peak area. The endothermic peak in the region 215-250°C due to loss of melting point of Polyacrlamide

(PAAm). This supports the formation of Gg-PAAm-02 hydrogel.

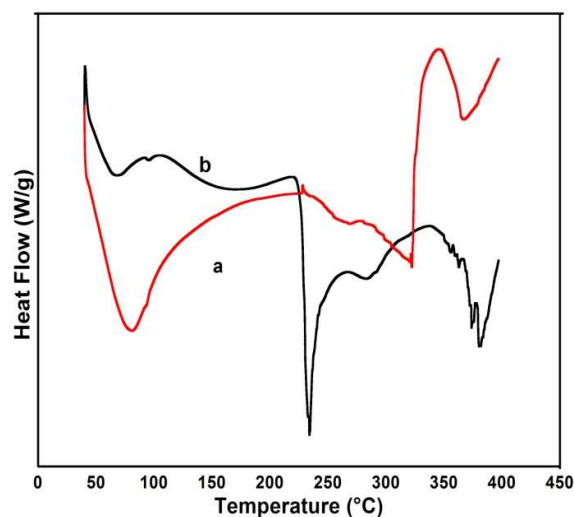


Fig. 2. DSC of Gg (a) and GG-PAAm-02(b)

Thermogravimetric Analysis (TGA)

Thermal analysis studies of Gg & Gg-AAm-02 were shown in Fig. 3. In the Gg sample, the initial weight loss of about 15% occurring in the range 50–150°C may be due to the loss of free and bound water molecules. A major weight loss of about 60% is observed between 200 and 400°C, This stage of degradation is attributed to the loss of hydroxyl group of Gg as water molecules. Very little weight loss occurs in the final stage leaving behind 25% of residual mass at 650°C. The thermal stability of Gg is affected on grafting and network formation, as indicated by the TGA of GG-PAAm-02 sample. It exhibits two-step degradation, the rates being highest between 150-280°C and 280-480°C, respectively. First step degradation attributed to the loss of hydroxyl group of Gg and second step degradation due to crosslinked chains of polyacrylamide in the grafted network. Similar results are reported in earlier studies [10].

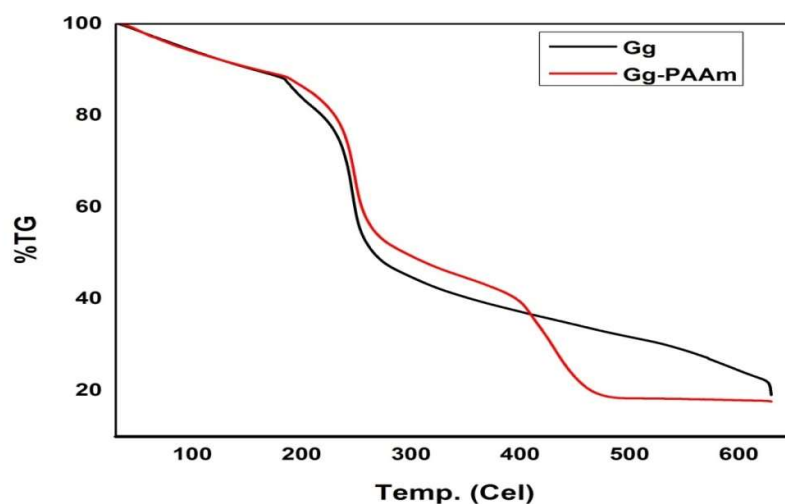


Fig. 3. TGA analysis of Gg & GG-PAAm-02 samples.

3.3 Scanning Electron Microscopic (SEM)

Scanning electron micrographs of Gg and crosslinked hydrogel are presented in Fig..4. The Gg polymer sample shows rough surface morphology Fig.(a). Gg-PAAm-02 crosslinker hydrogel Fig.(b). surface resulted in spherulite type of highly ordered polymer rearrangements in the guar gum. This may be because of one of the crosslinker help in polymer semicrystalline chain orientation and the later created nucleation regions to bind all the crosslinking polymer chains [11] in GG/PAAm grafted hydrogels. By seeing structure of morphology, smooth polymer rich surface.

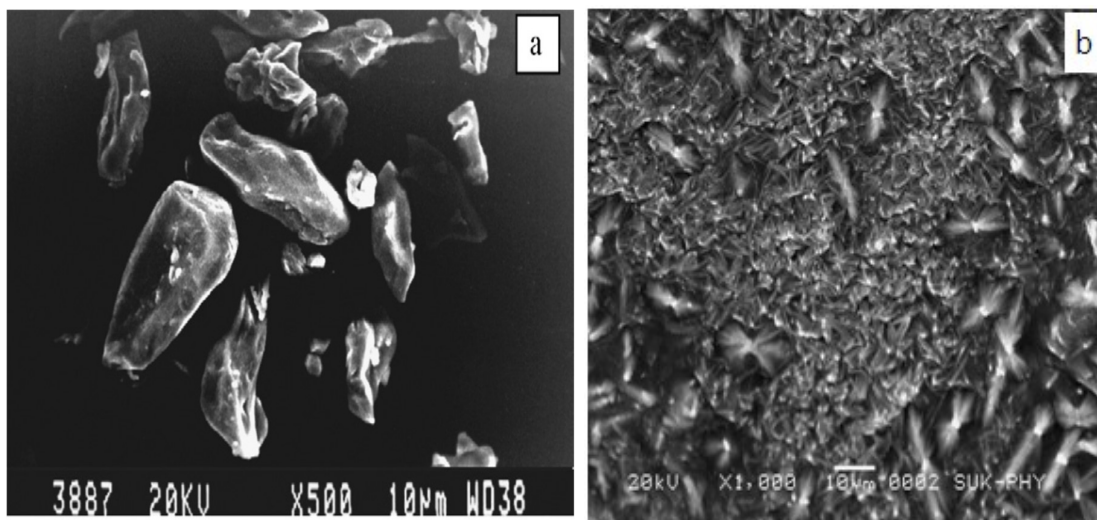


Fig.4. SEM analysis of (a) Guar gum, (b) Gg-PAAm hydrogel

3.4. Elemental analysis data:

The synthesis of Gg-PAAm network was achieved by polymerization of AAm in the presence of Gg by free radical polymerization along with simultaneous crosslinking namely, MBA. The grafting of AAm is expected to occur at the active site of Gg followed by crosslinking of the chains. In addition, a tight network structure is ensured by linking few repeating units of guar gum. The conclusive proof for this result comes from the elemental analysis data shown in Table 1. The % of N & % of C of Gg-PAAm sample reduces and % of H increases indicating Strong linkage between Gg & PAAm.

Sample code	% N	% C	% H
Gg	0.8	38.08	6.54
AAm	18.78	49.76	6.7
GG-PAAm-02	13.06	43.85	7.05

3.5. Swelling Studies:

3.5.1 Effect of the crosslinker on swelling of gels

From figure it has depicted that % SR decreases as increase crosslinker MBA concentrations (0.38 mol - 1.2 mol) in polymer hydrogel. Generally, the crosslinker concentration is directly related to the density of crosslinks in the gels [12]. At lower crosslinker concentration, the gel may have lower crosslinking density and hence higher swelling capacity. Whereas the gel formed with high crosslinker concentrations will possess higher crosslinking density causing a decrease in the distance between the crosslink points, thereby lowering the swelling capacity.

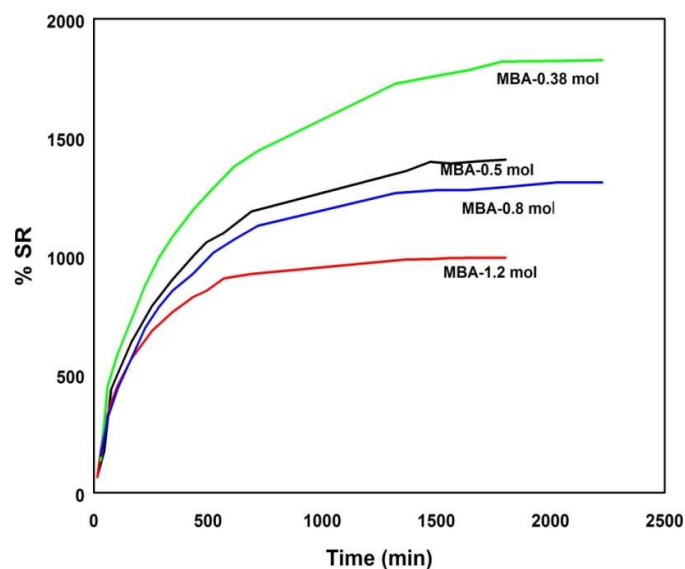


Fig.5. Swelling behaviour of Gg-PAAm of various concentration crosslinker MBA in aqueous medium

4.0 Conclusions

The free radical polymerizing of AAm in the presence of Gg and crosslinking agent resulted in firm network of PAAm grafted Gg structure. Swelling studies indicate as the optimum concentration of MBA for obtaining maximum swelling. With increase in MBA content the hydrophilicity of the polymer gel and hence the swelling appears to increase, counterbalancing the action of crosslinking. The crosslink density appears to be the deciding factor for controlling the swelling capacity of the presently studied IPN systems. Present synthesized hydrogel will have good application in drug release studies.

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