International Journal of Biological Macromolecules 80 (2015) 177–188

Contents lists available at ScienceDirect

International Journal of Biological Macromolecules

journal homepage: www.elsevier.com/locate/ijbiomac

A green approach to prepare silver nanoparticles loaded gum acacia/poly(acrylate) hydrogels

S.K. Bajpai*, Mamta Kumari

Polymer Research Laboratory, Department of Chemistry, Govt. Model Science College, Jabalpur, M.P. 482001, India

ARTICLE INFO

Article history:
Received 1 May 2015
Received in revised form 17 June 2015
Accepted 24 June 2015
Available online 27 June 2015

Keywords:
Gum acacia
Sodium acrylate
Clove
Silver nanoparticles

ABSTRACT

In this work, gum acacia (GA)/poly(sodium acrylate) semi-interpenetrating polymer networks (Semi-IPN) have been fabricated via free radical initiated aqueous polymerization of monomer sodium acrylate (SA) in the presence of dissolved Gum acacia (GA), using N,N′-methylenebisacrylamide (MB) as cross-linker and potassium persulphate (KPS) as initiator. The semi-IPNs, synthesized, were characterized by various techniques such as X-ray diffraction (XRD), thermo gravimetric analysis (TGA) and Fourier transform infrared (FTIR) spectroscopy. The dynamic water uptake behavior of semi-IPNs was investigated and the data were interpreted by various kinetic models. The equilibrium swelling data were used to evaluate various network parameters. The semi-IPNs were used as template for the in situ preparation of silver nanoparticles using extract of *Syzygium aromaticum* (clove). The formation of silver nanoparticles was confirmed by surface plasmon resonance (SPR), XRD and transmission electron microscopy (TEM). Finally, the antibacterial activity of GA/poly(SA)/silver nanocomposites was tested against *E. coli*.

1. Introduction

In the past decade, coinage metals based nanostructures have gained considerable importance due to their wide range of applications in electronics, agriculture, textile industry, biomedical field, etc. [1–3]. These nanostructures, particularly of silver and gold, have also shown strong antibacterial action against a number of bacteria, fungi etc. [4]. Recently, Haider and Kang [5] have reviewed preparation methods and applications of silver nanoparticles. Out of various approaches employed, metal nanoparticles are preferably synthesized via green chemistry based reduction approach. In recent past, several studies have been carried out to prepare silver nanoparticles via green chemistry approach. For example, Farhadi and his co-worker [6], investigated the synthesis of stable silver nanoparticles with the bio reduction method using two plants, one of which acted as a reducing agent and the other one as a stabilizing agent. An aqueous extract of soap-root (Acanthe phylum bracteates) was employed as a stabilizer and an aqueous extract of manna of hedysarum was employed as a reductant). In another interesting work, Khalil et al. [7] prepared Ag nanoparticles using hot water olive leaf extracts (OLE) as reducing and stabilizing agent. The effect of extract concentration, contact time, pH and temperature on the reaction rate and the shape of the Ag nanoparticles were investigated. Most recently, leaf extracts of *Cycas circinalis*, *Ficus amplissima*, *Commelina benghalensis* and *Lippia nodiflora*, have been employed successfully to prepare silver nanoparticles [8]. Hydrogels are three dimensional crosslinked polymer networks which have tendency to absorb appreciable quantity of water. Due to their soft and rubbery nature, they resemble human tissues. Their combination with metal nanoparticles has emerged out as a new class of materials that could be employed for a number of biomedical applications [9,10]. Although, there are a number of approaches to prepare polymer-metal nano-composites [11], the in situ approach has gained much popularity due to the fact that it enables one to obtain a uniform distribution of metal nanoparticles with controllable size within the polymer matrix [12,13].

Gum Arabic (GA), obtained from acacia tree, is a biocompatible, nontoxic and water soluble polysaccharide. This branched polymer consists of a backbone of 1,3 linked β-D-galactopyranosyl units and side chains contain two to five 1,3 linked β-D-galactopyranosyl units, joined to the main chain by 1,6 linkages [14]. Since it is inexpensive and nontoxic, it is widely used in food industry as a stabilizing, emulsifying and thickening agent. The other major applications include confectionery, beverage or liquid flavor emulsions, pharmaceuticals, cosmetic products, inks, etc. In the European list of permitted food additives, GA is classified as E 414. The Joint WHO/FAO Expert Committee on Food Additives has declared gum acacia as ADI-non specified (Acceptable Daily Intake), i.e. no quantitative limitation is stated and as such it is a nontoxic additive for human consumption [15]. This bio-polymer has a

---

* Corresponding author. Tel.: +91 9993220651.
E-mail address: sunil.mnlbpi@gmail.com (S.K. Bajpai).

http://dx.doi.org/10.1016/j.ijbiomac.2015.06.048
0141-8130/

number of biomedical applications also. For example, Varaprasad et al. [16] have investigated release of bio phosphate from crosslinked gum acacia hydrogels for gastrointestinal regions. Similarly, Singh et al. [17] have reported slow release of drug gentamycin from a hydrogel wound dressing composed of gum acacia and carbopol.

Since gum acacia is a non-toxic and biocompatible polymer, its hydrogel matrix can serve as an efficient nanoreactor for the in situ synthesis of silver nanoparticles. However, preparation of gum acacia hydrogel with well-defined crosslinked network is not reported till date. The reason is that GA molecule does not have a suitable functionality (as exist in vinyl monomers), which could transform it into three dimensional crosslinked networks. As an alternative method, a well-defined crosslinked network of a vinyl monomer may be prepared in the presence of gum acacia to yield a semi-interpenetrating network (IPN) which could serve as a template for silver ions to prepare polymer silver nanocomposites. Following this approach, we hereby report formation of crosslinked poly(sodium acrylate) network in the presence of dissolved GA to yield GA/poly(SA) semi-IPN. The polar sites, present in the hydrogel network act as nano-reactors to carry out clove-bud extract induced in situ reduction of pre-loaded Ag(I) ions within the matrix. Clove (*Syzygium aromaticum*) is one of the most valuable spices that has been used for centuries as food preservative and for many medicinal purposes. This plant represents one of the richest sources of phenolic compounds such as eugenol, eugenol acetate and gallic acid [18].

2. Materials and methods

2.1. Materials

Gum acacia (GA), monomer sodium acrylate (SA), cross linker N,N′-methylene bisacrylamide, initiator potassium persulphate (KPS), and silver nitrate ($AgNO_3$) were purchased from HiMedia Chemicals, Mumbai, India. Clove buds were obtained from a local medical store. The distilled water was used throughout the investigations.

2.2. Methods

2.2.1. Preparation of GA/poly(SA) semi-IPNs

The semi-IPNs were prepared by free radical polymerization of monomer SA in the presence of dissolved GA. In brief, a pre-calculated quantity of GA was dissolved in distilled water under moderate stirring for 30 min to ensure complete dissolution. Thereafter, definite amounts of monomer SA, cross linker MB and initiator KPS ware added and the reaction mixture was stirred vigorously to obtain an almost clear transparent solution. The total volume of the reaction mixture was made to 10 mL, transferred into test tube (Borosil, id 16 mm) and then put in an electric oven (Tempstar, India) at 60 °C for a period of 2 h. After polymerization was over, hydrogel was taken out, cut into slices with a knife and then put in refreshing distilled water for a period of 12 h to ensure complete leaching of unreacted chemicals. Finally, the hydrogels were dried in a vacuum chamber till constant weight and kept in an air tight poly(propylene) container for further use. In all, five samples with varying compositions were prepared (please see Table 1).

2.2.2. Gel fraction of semi-IPNs

The gel fractions were determined by a method reported elsewhere [19]. The dry samples were extracted in distilled water at 30 °C for 48 h to remove the soluble part and then dried again. Their percent Gel Fraction (GF) was determined using following formula:

$$(\%)\,\mathrm{GF} = \frac{W_2}{W_1} \cdot 100 \qquad (1)$$

where W_2 and W_1 are the weights of the dry samples after and before extraction.

2.2.3. Extraction of clove oil from clove buds

In order to prepare clove extract (CE), a definite quantity of clove buds were mixed into 100 mL of distilled water and kept for a period of 48 h under normal stirring. Finally, the clove buds were filtered out and the filtrate was collected in an amber colored bottle and stored in dark to avoid any possible effect of light. Fig. 1(a) and (b) shows optical images of clove buds and clove extract respectively.

2.2.4. Formation of silver nanoparticles in solution by clove extract

In a beaker (Borosil, 100 mL), 0.117 mmol of $AgNO_3$ was dissolved in 25 mL of distilled water. Now 6 mL of this solution was diluted to 12 mL, followed by addition of 1 mL of clove extract (CE) under normal stirring. The mixture was exposed to microwaves in a microwave oven (LG, model, USA) for 4–5 cycles, each cycle consisting of 5 s. The solution turned light brown, thus indicating formation of Ag NPs.

2.2.5. Surface plasmon resonance (SPR) of Ag NPs

The absorbance of aqueous solution of silver nanoparticles was recorded using Genysis, Spectrophotometer.

2.2.6. Preparation of GA/poly(SA)/Ag nanocomposites

The in situ reduction of Ag(I) was carried out within the swollen hydrogel matrix. For this, silver nitrate solution of definite concentration was prepared and a representative hydrogel sample HG1 was equilibrated in it for a period of 12 h. Now, the Ag(I) ions loaded hydrogel was transferred into clove extract (CE) for a period of 12 h at 37 °C. The brownish appearance of hydrogel indicated the formation of silver nanoparticles within the hydrogel.

2.2.7. Characterization of hydrogels

The Fourier Transform Infrared (FTIR) spectra were recorded with an FTIR spectrophotometer (Shimadzu, 8400, Japan) using KBr. The powdered sample was mixed with KBr. The scans recorded were the average of 100 scans and the selected spectral range between 400 and 4000 cm^{-1}.

The X-ray diffraction (XRD) method was used to measure the crystalline nature of plain and silver nanoparticles loaded hydrogels. These measurements were carried out on a Rikagu Diffractometer (Cu radiation = 0.1546 nm) running at 40 kV and 40 mA. The diffractogram was recorded in the range of 2 from 3 to 50° at the speed rate of 2°/min.

The TG analysis was performed using a thermo gravimetric analyzer (Mettler Toledo TGA/SDTA 851, Switzerland), with temperature range of 30–800 °C, heating rate of 10 °C min^{-1} and N_2 flow rate of 30 mL min^{-1}.

The transmission electron microscopy (TEM) was used to find out the size of AgNPs inside the nano-composite. To image the Ag NPs, the hydrogel-silver nano composite was grinded to fine particles and equilibrated in distilled water for a period of 72 h, followed by ultra-sonication at a high revolution speed (Rivotech, India). As a result, some of the Ag NPs came out from polymer network into the aqueous phase. A few drops of this aqueous dispersion were dropped on a copper grid and allowed to dry at room temperature. The copper grid was inserted into JEOL-1210 TEM (JEOL, Tokyo, Japan) (operating at 60 kV) operating at an acceleration voltage