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Functionalization of natural gum: An effective method to prepare iodine complex

Syed Ishraque Ahmad[a,b,*], Nasreen Mazumdar[a], Sunil Kumar[c]

[a] Department of Chemistry, Zakir Husain Delhi College, University of Delhi, New Delhi 110002, India
[b] Department of Chemistry, Jamia Millia Islamia University, New Delhi 110025, India
[c] Defence Materials and Stores Research and Development Establishment, Kanpur 208013, India

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ABSTRACT

To overcome the drawbacks associated with iodine e.g. insolubility in water, etc., it has been complexed with polymers that have the ability to bind it. In this study, gum arabic (GA), a natural gum was functionalized to introduce new reactive groups that can easily interact with small molecules followed by iodination in ethanol solution to prepare an iodine complex. The samples were characterized by FTIR, thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC). The synthesized iodine complex was found reddish-brown in colour and stable at room temperature. The interaction of free available iodine with functionalized GA was also studied and established by UV–vis spectrophotometer. The amount of iodine released in water was measured by iodometric titration method and its value compared with the available iodine complex, polyvinylpyrrolidone–iodine complex. The antimicrobial activity of iodine complex was tested against *Escherichia coli* (Gram negative bacteria) and found to be effective against it.

1. Introduction

Development of functionalized polymer is a promising field of research that has attracted the attention of scientific community because of their potential for a much wider range of applications. Besides the application in the fields of optics and electronics, functionalized polymers have been used as hydrogels and stimulus-responsive polymers in various biomedical fields such as surgical sutures, dental fillings, wound dressing, bone cements and hollow fibres for dialysis. Functionalization of water soluble polymers has the key advantage of introducing several reactive groups, such as hydroxyl, carboxyl and amine that can easily interact with small molecules (Garcia & Vidal, 2000). The important applications of functionalized polymer include their usage particularly in the field of medicine. Both synthetic and natural polymers have been functionalized by various researchers using different functionalizing agents. Natural polymers such as protein and carbohydrates (cellulose and starch) are generally degraded in biological systems by hydrolysis followed by oxidation (Yukuta, Akira, & Masatoshi, 1990) The functionalization of natural polymers, especially polysaccharides has been widely used because of their unique advantages as they are usually non-toxic, biocompatible, biodegradable and abundant (Coviello, Matricardi, Marianecci, & Alhaique, 2007). Xu, Miladinov, and Hanna (2004) carried out acetylation of starch using acetic anhydride and sodium hydroxide to produce a controlled release system. A lowly substituted acetyl agarose product was developed by dispersing agarose in acetic anhydride and pyridine at room temperature to form a controlled drug release system (Garcia & Vidal, 2000). Super adsorbent hydrogels were synthesized by the chemical modification of gum arabic (GA) via grafting with acrylic monomers (Zohuriaan-Mehr, Motazedi, Kabiri, Ershad-Langroudi, & Allahdadi, 2006). Chemically modified GA treated with sodium persulfate was developed as a hydrogel for drug delivery (Favaro et al., 2008).

Though much works has been done on the study of interaction of small molecules with functionalized natural polymer, no one has reported the synthesis of functionalized GA based iodine complex. Since iodine is a powerful antimicrobial agent (Ellis & Vree, 1989) and free iodine is a toxic, irritant and physiologically active, its use is restricted in various biomedical applications. These restrictions can be minimized by attaching iodine to functionalized polymers (Siggia, 1957). Although several researchers have synthesized polymer–iodine complexes from both synthetic and natural polymers using molecular and ionic iodine, the understanding of the chemistry of interaction of iodine with functionalized polymer is indeed a subject of considerable interest. These polymer–iodine complexes are of considerable importance because of their antimicrobial and disinfecting properties and are widely used in medical fields for both external and internal purposes (Chen & Wang, 2001; Chetri, Dass, & Sarma, 2007; Morain & Vistnes, 1977; Punyani & Singh, 2006; Rendleman, 2003; Ribeiro et al., 2006; Schenck,

* Corresponding author. Tel.: +91 9560062872.
E-mail addresses: ahmad.ishraque@gmail.com, ishraque.ahmad@gmail.com (S.I. Ahmad).

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Simak, & Haedicke, 1979; Shelanski & Shelanski, 1956; Siggia, 1957; Singhal & Ray, 2002; Wang & Easteal, 1999; Xing, Deng, & Yang, 2005). The most extensively studied polymer–iodine complex is polyvinylpyrrolidone–iodine complex which is a combination of iodine with polyvinylpyrrolidone (PVP), introduced by Shelanski and Shelanski (1956). Chen and Wang (2001) prepared the cyclodextrin–chitosan grafted copolymer and treated it with radioactive iodine to synthesize the polymer–iodine inclusion complex. Other reports on the studies of iodine interaction with polysaccharides include iodine absorption by structurally modified dextran, chitin and chitosan, ethyl cellulose and starch (Chang & Morris, 1953; Ignatova, Manolova, & Rashkov, 2007; Tyagi, Singh, & Singh, 2000; Xing et al., 2005).

Iodine undergoes a number of reactions in aqueous solution including hydrolysis, dissociation, disproportionation and complex formation (Gottardi, 1999). Consequently in aqueous solution iodine is present in different forms (Gottardi, 1999): I_2, HOI, OI^-, H_2OI^+, I_3^-, IO_3^- and I^-. The equilibrium concentrations of these forms are determined in pure aqueous solutions. According to Chang (1958), the main forms of iodine at pH 5–7 are I_2, HOI and I^-. However, this may not be the case when iodine is complexed with a polymer (Gottardi & Fresenius, 1983) such as PVP and polysaccharides. Therefore, for polymer–iodine complex only the triiodide and the interactions of the iodophoric molecules with I_2, I_3^- and I^- are of importance.

The objective of the present study is to develop an iodine complex based on functionalized GA without a significant loss of germicidal efficacy of iodine with added advantage of its easy availability and low cost. Besides the thermal stability and interaction of available free iodine with carbonyl groups of functionalized GA have been studied in detail. The amount of available free iodine released in water by functionalized GA based iodine complex has been compared with PVP–iodine complex by titrimetric method.

2. Materials and methods

2.1. Materials

Gum arabic, acetic anhydride, ethanol, carbon tetrachloride and sodium hydroxide were supplied by Merck (India) Limited. Iodine resublimed LR and ethylcellulose (EC) were purchased from S.D. Fine-CHEM Ltd., India. The PVP–iodine complex was purchased from Sigma, USA.

2.2. Acetylation of gum arabic

GA was acetylated with the same process of acetylation of starch as followed by Xu et al. (2004). 3.25 g of GA was mixed with acetic anhydride at a weight ratio of 1:4 in a 100 ml round bottom flask to obtain the maximum yield of acetylated product. After stirring the mixture for 30 min at 80 °C, 10 ml of 50% (w/v) aqueous solution of sodium hydroxide was added that acts as a catalyst. The reaction was carried out for different time periods (30, 60 and 120 min) at 80 °C. Excess of ice was added to the reactor to terminate the reaction. The acetyl derivative of GA was obtained as the creamy white solid and dried at about 50 °C.

2.3. Iodination of acetylated gum arabic (AGA)

4 g of acetylated gum arabic (AGA) powder obtained by acetylating GA for 120 min was mixed with 25 ml of different concentrations of molecular iodine solutions prepared in ethanol (2, 3, and 4%, w/v) in a 50 ml round bottom flask. The heterogeneous mixtures were stirred at room temperature for 2 h. The reddish brown solid was separated and thoroughly washed with ethanol to remove the loosely bound iodine. The products were dried in air at room temperature.

2.4. Characterization

2.4.1. Determination of degree of substitution (DS) in AGA

Degree of substitution (DS) in AGA has been determined by standard method (Xu et al., 2004) available in the literature. The selected samples of acetyl derivative of GA acetylated for different periods of time (30, 60 and 120 min) were coded AGA-1, AGA-2 and AGA-3, respectively. GA was reacted with acetic anhydride for different periods of time to convert the polysaccharide into its acetyl derivative. The different degrees of substitution were determined by the following method.

An exact weight (0.5 g) of AGA powder was taken in a 250 ml conical flask containing 50 ml distilled water. The pH of the solution was adjusted to 7.0 with 0.02 N hydrochloric acid. Next 25 ml of 0.5 N NaOH was added and the mixture was heated on a hot plate until a transparent solution was obtained. The solution was titrated against HCl (0.02 N) to determine the amount of NaOH present in excess and bring the pH back to 7.0. DS was calculated using the following equation (Xu et al., 2004):

$$\mathrm{DS} = 162 \times \frac{N_1V_1 - N_2V_2}{1000} \times W - 42(N_1V_1 - N_2V_2)$$

where N_1 is the normality of NaOH, V_1 is the volume of NaOH, N_2 is the normality of HCl, V_2 is the volume of HCl and W is the weight of the sample (g). A mean value of DS for each sample was calculated from a set of three readings.

2.4.2. FTIR spectroscopy

FTIR spectra of GA, acetylated derivatives of GA with different degrees of substitution (AGA-1, AGA-2 and AGA-3) and iodine complexes of AGA-3 prepared using different concentrations of iodine–ethanol solutions (AGA3-1·I_2, AGA3-2·I_2, AGA3-3·I_2) were recorded on a Nicolet Impact 400, FTIR spectrophotometer (Madison, WI, USA). The FTIR spectra were analysed and compared to study the acetylation reaction of GA and understand the interaction of iodine with the acetyl groups of AGA.

2.4.3. Thermogravimetric analysis (TGA)

Thermogravimetric (TG) studies of GA, AGA-3 and AGA3-3·I_2 were carried out by recording their thermograms in TGA Q50 (TA Instruments, New Castle, USA) over a temperature range of 0–500 °C at a heating rate of 10 °C/min in nitrogen atmosphere. TG thermograms were used to determine and compare the thermal stability of GA post-acetylation and the effect of iodination on the thermal stability of AGA-3.

2.4.4. Differential scanning calorimetry (DSC)

Differential scanning calorimetry (DSC) studies of GA, AGA-3 and AGA3-3·I_2 were performed on DSC Q200 (TA Instruments, New Castle, USA) over a temperature range of 0–160 °C at a heating rate of 10 °C/min in nitrogen atmosphere. The DSC plots were analysed to estimate the changes in thermal properties in GA and AGA-3 after acetylation and iodination respectively.

2.4.5. UV–vis spectroscopy

Dilute aqueous solutions of molecular iodine, I_2 and its other forms such as iodide ion, I^- and triiodide ion, I_3^- were prepared and their UV–vis scans were recorded in a Perkin-Elmer spectrophotometer EZ-221 (Waltham, MA, USA) from 200 to 600 nm to determine the peak intensity and λ_{max} values of the iodine species.