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

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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,

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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.

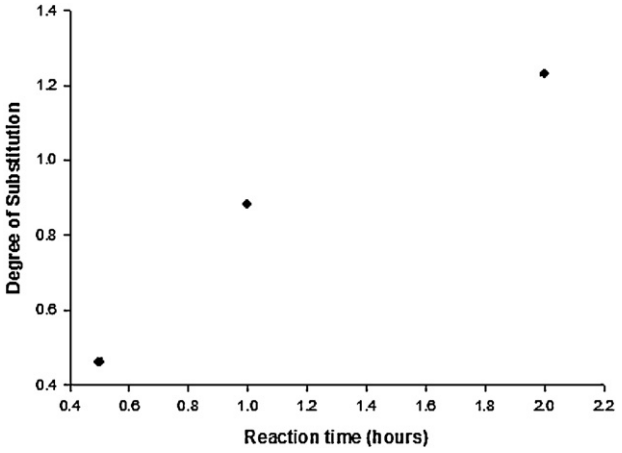


Fig. 1. Degree of substitution (DS) in acetylated GA is plotted against acetylation reaction time.

2.4.6. Iodometric titration

The amount of available iodine in water from the polymer–iodine (AGA3-3·I_2) powder (weighing 500 mg) was compared with polyvinylpyrrolide–iodine complex of same weight estimated by iodometric titration. The method involved titration of liberated iodine with 0.005 N standard sodium thiosulfate solution using starch as indicator. The samples were suspended in 50 ml water in a closed iodine flask (100 ml) for 24 h. Released iodine was titrated against freshly prepared 0.005 N sodium thiosulfate solution already standardized with potassium dichromate solution.

2.4.7. Antimicrobial activity by zone of inhibition method

To study the antimicrobial activity of polymer–iodine complex (AGA3-3·I_2) powder, zone of inhibition method was used. Double layered Luria agar plate was prepared and inoculated with *Escherichia coli* (Gram negative) bacterium. Since *E. coli*, though being a Gram negative bacterium, has an outer membrane in addition to a cell membrane, whereas Gram positive bacterium contains cell membrane only. It was selected for this study. A weighed amount of AGA3-3·I_2 powder (10 mg) was poured into the plate using a sterile cut tip of a funnel. A non-iodinated AGA-3 powder was also placed in the plate as control. The plate was then incubated at 37 °C for overnight and the clear zone around the sample was measured the next day as a measure of antimicrobial activity of the polymer–iodine complex (AGA3-3·I_2) powder.

3. Results and discussion

3.1. Degree of substitution (DS)

The results of hydrolysis of AGA samples are presented in Fig. 1. The calculated DS values for AGA-1, AGA-2 and AGA-3 were 0.46, 0.88 and 1.23 respectively. The values showed that as acetylation of GA progressed from 30 min to 120 min, more and more —OH groups were converted into —$OCOCH_3$ groups. The sample AGA-3 with the highest number of acetyl groups (DS 1.23) was chosen for iodination as iodine was expected to react with the)C=O of acetyl groups.

3.2. FTIR spectroscopy

Fig. 2 presents the FTIR spectra of GA, AGA-1, AGA-2 and AGA-3 and Fig. 3 presents the spectra of AGA-3 and its different iodinated products containing different concentrations of iodine, AGA3-1·I_2, AGA3-2·I_2 and AGA3-3·I_2. The IR spectra of GA, AGA-1,

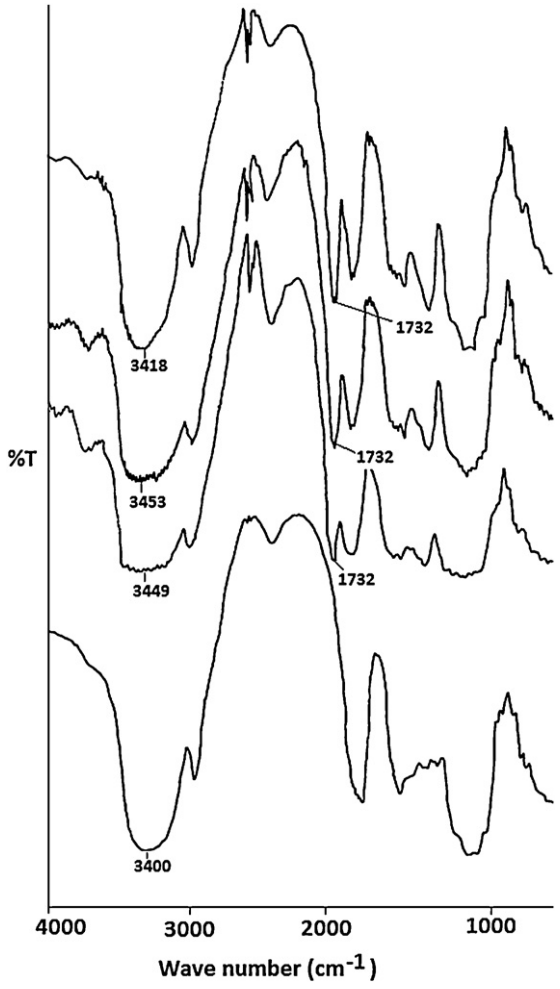


Fig. 2. FTIR spectra of (a) GA, (b) AGA-1, (c) AGA-2 and (d) AGA-3.

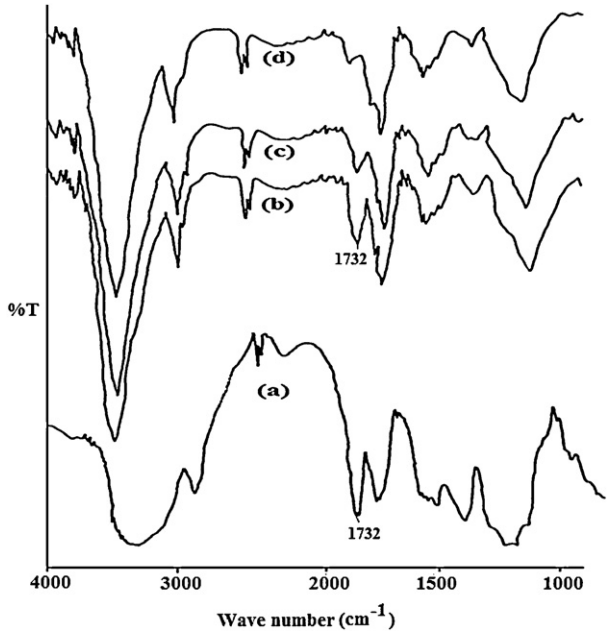
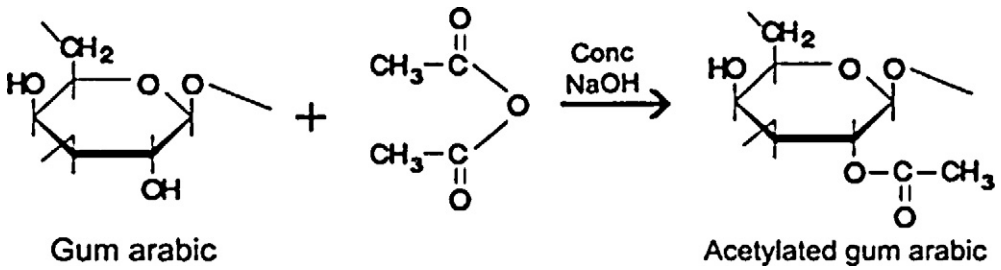
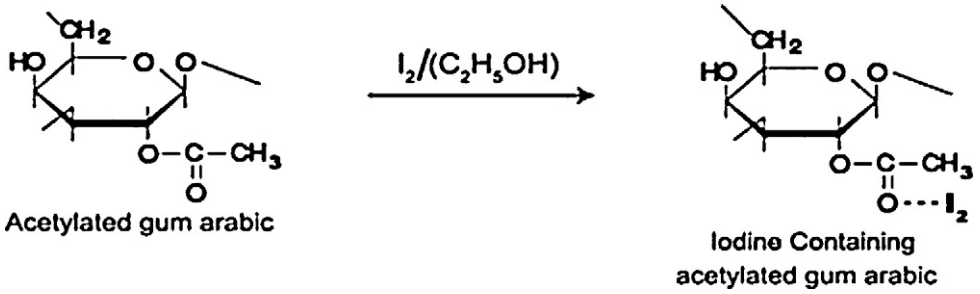


Fig. 3. FTIR spectra of (a) AGA-3; and its iodine complexes prepared using different concentrations of iodine/ethanol solutions (b) 2% (c) 3% and (d) 4% I_2/EtOH.



Scheme 1. Acetylation reaction of gum arabic.



Scheme 2. Interaction between iodine and ⟩C=O groups of gum arabic.

AGA-2 and AGA-3 show —OH absorption at 3400 cm^{-1}, 3449 cm^{-1}, 3453 cm^{-1} and 3418 cm^{-1} respectively; a new peak at 1732 cm^{-1} was observed in the spectra of all the acetyl derivatives of GA. The sharp peak at 1732 cm^{-1} indicates the presence of a ⟩C=O group that appears due to the substitution of —OH by $OCOCH_3$ during the acetylation reaction (as shown in the reaction Scheme 1). It was also observed that the intensity of ⟩C=O absorption in the spectra of AGA samples increased with increase in the acetylation reaction time. This shows different degrees of substitution in GA. The ⟩C=O absorption intensity decreased after iodination of AGA-3. This explains the proposed interaction of iodine with ⟩C=O groups of AGA-3. Also there was a decrease in the intensity of ⟩C=O peak in the spectra of iodine complexes of AGA-3 prepared with increasing concentration of iodine reactant and this is probably due to a higher extent of reaction between available iodine and the acetyl groups of AGA (presented in reaction Scheme 2).

3.3. Thermogravimetric analysis (TGA)

Fig. 4 presents TGA curves of GA, AGA-3 and AGA3-3·I_2. The thermal stability of pure GA was found to be much lower than that of AGA-3. The weight loss in the first stage of decomposition in the GA and AGA-3 samples might have taken place due to the loss of residual moisture in the polymer samples and that was why the initial decomposition temperature for the first stage (IDT_1) was mostly the same (~70 °C) for GA and AGA-3. The initial decomposition temperature for second stage (IDT_2) of GA increased from 95 °C to 209 °C and 50% weight loss of the sample occurred at 315 °C compared to 82 °C for the GA after acetylation indicating an increase in thermal stability. The lower IDT_2 of GA has been basically due to inter- and/or intra-molecular dehydration of GA molecules with water as the main product of decomposition. The acetylation reaction of GA replaced the hydroxyl with acetyl groups and the process slowed down the condensation reaction thus increasing its thermal stability. A similar observation has been reported by Xu et al. (2004), who studied the acetylation of starch. The iodinated sample of AGA-3 (AGA3-3·I_2) showed a significant decrease in thermal stability. The first stage weight loss by AGA3-3·I_2 (3.5%) at 56 °C was lower than AGA-3, probably due to sublimation of iodine entrapped into the

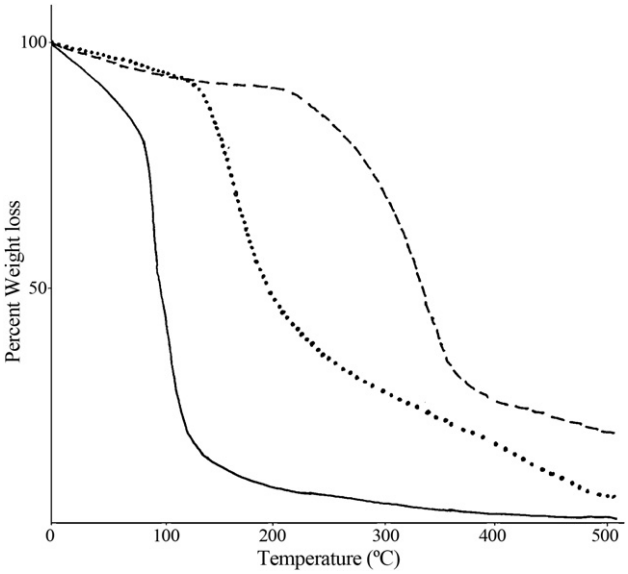


Fig. 4. TGA curves of (a) pure GA (—), (b) AGA-3 (----), and (c) AGA3-3·I_2 (. . .).

Table 1
Thermogravimetric data for GA, acetylated GA (AGA) and iodinated AGA.

Samples (°C)	IDT_1 (°C)	IDT_2 (°C)	IPDT	Temperatures (°C) at various weight losses		
				20%	50%	80%
GA	70	95	112.14	78	82	102
AGA-3	74	209	270	250	315	490
AGA3-3·I_2 (4%)	56	173	240	180	230	380

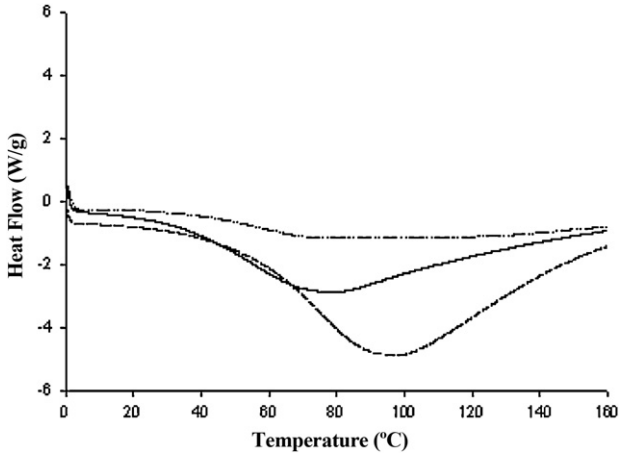


Fig. 5. DSC curves of (a) pure GA (—), (b) AGA-3 (----) and (c) AGA3-3·I_2 (-···-).

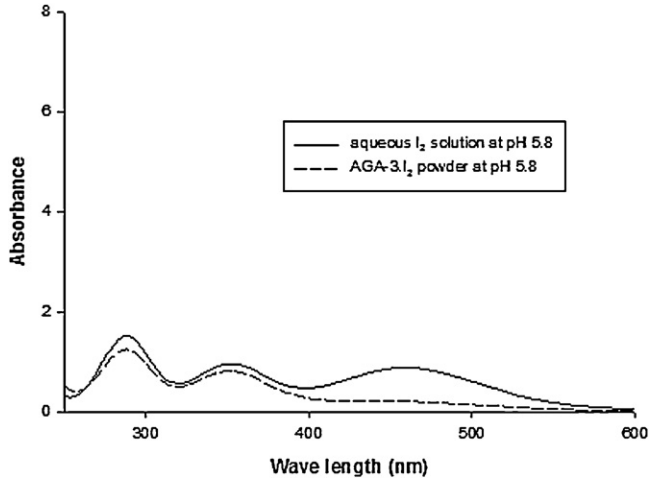


Fig. 6. UV–vis spectra of aqueous iodine (I_2) solution and iodine released from AGA3-3·I_2 powder at pH 5.8.

polymer matrix in addition to moisture loss. After iodination, IDT_2 of AGA-3 decreased from 209 °C to 173 °C and 50% weight loss of the sample occurred at 230 °C compared to 315 °C for the AGA-3, probably due to the sublimation of loosely absorbed iodine molecules. The calculated values of integral procedural decomposition temperatures (IPDT) for GA, AGA-3 and AGA3-3·I_2 also showed that the acetylated product, AGA-3 is thermally more stable than GA but its stability decreases after iodination. Table 1 presents the IPDT values of the samples.

3.4. Differential scanning calorimetry (DSC)

Fig. 5 shows the DSC curves of GA, AGA-3 and AGA3-3·I_2. The DSC curve of GA showed a very broad endothermic peak around 78 °C and can be related to the melting and partial thermal decomposition of the complex polysaccharide consisting of several sugar units present as branches and sub-branches. The thermal decomposition of GA below 100 °C interferes with the glass transition of the polymer. The DSC curves showed higher glass transition temperature (T_g) of AGA-3 (97 °C) than GA (78 °C). The increase in T_g of GA after acetylation may be attributed to the lowering of chain flexibility due to the presence of heavier acetyl groups in the acetylated sample. The T_g of AGA-3 (97 °C) decreased to 76 °C after iodination in iodine–ethanol solution, which is even lower than the T_g of GA, probably due to the sublimation of absorbed iodine molecules that confirms the molecular iodine interaction with the carbonyl groups of AGA-3.

3.5. UV–vis spectroscopy

Water containing released iodine from polymer–iodine (AGA3.3–I_2) powder (weighing 500 mg) was scanned in a UV–vis spectrophotometer from 200 to 600 nm to check the release of different iodine forms in water. UV–vis spectra of aqueous iodine solution (65 mg of molecular iodine was dissolved in 50 ml of water) at pH 5.8 and released iodine solution from AGA3-3·I_2 powder (500 mg powder containing 65 mg iodine) in 50 ml of water at same pH were scanned from 250 nm to 600 nm (below 250 nm, the noise was produced due to high concentration of iodine in the aqueous solution) without dilution of both the solutions and compared to determine the interaction of molecular iodine with carbonyl group of AGA-3.

Considering Gottardi's (1999) study of stability of molecular iodine in the aqueous solution at pH5.8. UV–vis spectra of aqueous iodine solution (65 mg of molecular iodine was dissolved in 50 ml of water) at pH 5.8 and released iodine solution from AGA3-3·I_2 powder (500 mg powder containing 65 mg iodine) in 50 ml of water at same pH were studied as shown in Fig. 6. UV–vis spectrum of aqueous iodine solution showed three peaks corresponding to I_3^- (288 nm and 351 nm) and I_2 (460 nm) as observed by Gazda, Lipert, Fitz, and Porter (2004). Although two peaks at 288 nm and 351 nm corresponding to I_3^- were found in released iodine solution from AGA3-3·I_2 powder, the peak at 460 nm corresponding to free molecular iodine was observed with very low absorbance. It was reported that iodine shows a strong tendency to form charge transfer complexes even with the weak electron donors (Bhagat et al., 2008). UV–vis spectra of aqueous iodine solution and released iodine solution from AGA3-3·I_2 powder at pH 5.8 were scanned to determine the interaction of molecular iodine with carbonyl group of AGA-3. Since AGA-3 was iodinated with iodine–ethanol solution (containing mostly molecular iodine), the decrease in absorbance of peak at 460 nm corresponding to I_2 in the aqueous solution of released iodine from AGA3-3·I_2 powder indicated the formation of iodine complex of AGA-3 due to the interaction between molecular iodine and carbonyl group of AGA-3. The release study of iodine from AGA3-3·I_2 powder also confirms the proposed structure of iodinated AGA-3 as mentioned in reaction Scheme 2.

3.6. Iodometric titration

Titrimetric method was used to determine the amount of available iodine released from AGA3-3·I_2 powder which was then compared with PVP–iodine complex. The amount of available iodine from AGA3-3·I_2 powder (500 mg powder containing 65 mg iodine) was calculated to be 17.08%, which shows polymer–iodine interaction. Similar result was also obtained with PVP–iodine complex that contains 13.5% of available iodine as estimated by titrimetric method which is nearly equal to the reported value (12%).

3.7. Antimicrobial activity by zone of inhibition method

A clear zone of 15 mm diameter was observed around the iodinated sample in the plate inoculated by *E. coli* as shown in Fig. 7. A non-iodinated AGA-3 placed on the agar plate as control was found completely surrounded by bacterial colonies.

The appearance of a clear zone around the AGA3-3·I_2 powder indicates the absence of bacterial colonies around the iodinated sample. This indicates the antimicrobial role of the AGA3-3·I_2 powder.

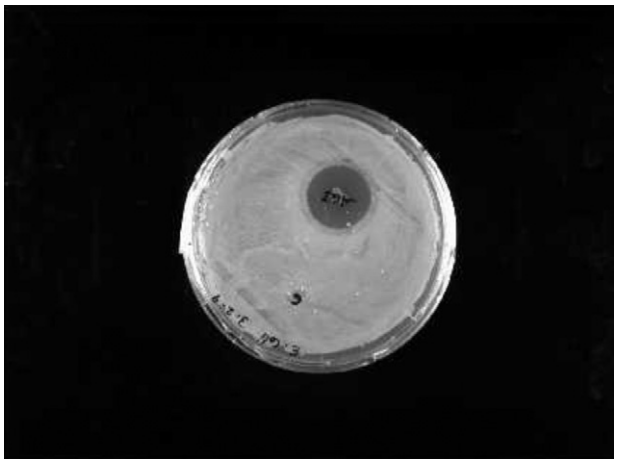


Fig. 7. Zone of inhibition around AGA3-3·I_2 in *E. coli* powder at pH 5.8.

4. Conclusions

Functionalization of GA followed by iodination in ethanol solution to prepare a stable iodine complex proceeded well. The results of various studies showed an interaction between molecular iodine and ⟩C═O groups of AGA-3 that affected the thermal property and release profile of functionalized GA based iodine complex. Amount of available iodine in water released from AGA3-3·I_2 powder was found comparative with PVP–iodine complex that contains 13.5% of available iodine as estimated by titrimetric method, suggesting that functionalized GA based iodine complex could be used for similar applications.

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