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Grafting of *N*-vinyl-2-pyrrolidone onto κ-carrageenan for silver nanoparticles synthesis

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ABSTRACT

A water soluble, non-gel, poly (*N*-vinyl-2-pyrrolidone)/κ-carrageenan (PVP/KC) hybrid was synthesized by graft copolymerization of *N*-vinylpyrrolidone (VP) onto κ-carrageenan in an aqueous medium using ammonium persulphate (APS) as an initiator. Factors affecting the polymerization reaction such as ammonium persulfate concentration, reaction temperature and time, liquor to KC ratio (LR) and KC to VP molar ratio were studied. The results obtained revealed that the optimum reaction polymerization conditions to prepare that hybrid with a total conversion of 93.9% are: [VP], 0.1799 mol/L; VP/KC molar ratio, 50%; [APS], 0.0105 mol/l; LR, 15 l/k; reaction temperature, 90 °C and reaction time, 75 min. Moreover, the grafted KC of that hybrid was characterized via investigating its FTIR analysis. Furthermore, the potential application of such hybrid as a route for synthesis of silver nanoparticles (Ag NPs) using $AgNO_3$ as a precursor was investigated. The synthesized Ag NPs are characterized using the ultraviolet-visible spectroscopy (UV–vis) as well as transmission electron microscope (TEM). The UV–vis showed a band at 435 nm that confirms the presence of Ag NPs. The TEM image shows that such nanoparticles have a spherical structure with an average size ranging from 3 −18 nm.

1. Introduction

Carrageenans are nontoxic biodegradable water soluble gums that are found in certain species of some red seaweed families. Chemically, they composed of sulfated linear polysaccharides of D-galactose and 3,6-anhydro-D-galactose. According to the variation in disaccharide-repeating units, carrageenans are named in Greek-letter prefixes as mu-, kappa-, nu-, iota-, and lambda-, theta-, and xi-carrageenans. Both the charged nature of the sugar units and their structural arrangement within the macromolecule render the carrageenans chemically reactive and interpret for the ability to form gels. Kappa-carrageenan consists of alternating 1,3-linked β-D-galactose-4-sulfate and 1,4-linked 3,6-anhydro-α-galactose residue. It is used mainly for its gelling properties (Campo, Kawano, da Silva, & Carvalho, 2009; Necas & Bartosikova, 2013; Zia et al., 2017). According to their suspending, thickening, and gelling properties carrageenan is used in many industrial applications such as food, pharmaceutical and toilet goods, ceramics, coatings, etc, (Campo et al., 2009; Necas & Bartosikova, 2013).

On the other hand, poly (*N*-vinyl-2-pyrrolidone) (PVP) has unique chemical and physical properties. It is a nontoxic synthetic water-soluble polymer finds applications as a film former, binder, protective colloid and suspending agent, stabilizer, and complexing agent (Fahmy, 2009; Fahmy, Abo-Shosha, & Ibrahim, 2009). Furthermore, PVP has strong affinity for silver and some metal oxide nanoparticles such as ZnO and TiO_2 nanoparticls (Fahmy, Eid, Hashem, & Amr, 2013).

In the recent years, silver nanoparticles (Ag NPs) have attracted a lot of attention due to their good conductivity, chemical stability, catalytic action and anti-bacterial properties. Ag NPs can be incorporated into a lot of medical products, cosmetic products, composite fibers, biosensor materials, super-conducting materials, and electronic components (Abdel-Mohsen et al., 2017; Abou-Okeil, Sheta, Amr, & Ali, 2012; Iravani, Korbekandi, Mirmohammadi, & Zolfaghari, 2014; Montaser et al., 2016; Natsuki, Natsuki, & Hashimoto, 2015; Sharma, Sharma, & Singh, 2017). Several physical and chemical methods have been used for synthesizing Ag NPs. The most popular chemical methods include chemical reduction of silver ions using a variety of organic and inorganic reducing agents, physicochemical reduction, electrochemical techniques, and irradiation methods. The most problems in synthesis of Ag NPs are the stability and aggregation of the produced NPs, control of crystal growth, morphology, size and size distribution (Abdel-Mohsen, Aly, Hrdina, & El-Aref, 2012; Abou-Okeil, Sheta et al., 2012; Iravani et al., 2014; Natsuki et al., 2015; Sharma et al., 2017).

Polymer composites containing Ag NPs are important materials as they possess novel applications.The used polymers can act as reducing agent and as stabilizing agent whereas the proper functional group containing polymers can reduce the metal ions to atoms (Abou-Okeil,

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2012; Sagitha, Sarada, & Muraleedharan, 2016). Earlier study reported that nanocomposite of poly(methyl methacrylate) with Ag NPs wasprepared using an in-situ radical polymerization technique, where the reduction of Ag^+ precursors takes place during the reaction. The initiator efficiency was decreased by the presence of the Ag NPs, leading to a decreasing in the reaction rate (Siddiqui et al., 2015). In another study poly(methacrylic acid)/silver nanoparticles composite was synthesized in-situ as corrosion inhibitor for mild steel (Solomon, Umoren, & Abai, 2015). Copolymers like cyclodextrin graft poly acrylonitrile were used to prepare Ag NPs. The copolymer reduces the silver ions and stabilizes the produced Ag NPs (Fanta, 1973; Hebeish, Higazy, AbdelHady, & Sharaf, 2016).

In the current research work, graft copolymerization of N-vinylpyrrolidone onto κ-carrageenan was carried out in an aqueous medium using ammonium persulphate as an initiator to form water soluble, non-gel, poly (*N*-vinyl-2-pyrrolidone)/κ-carrageenan hybrid that can find a potential application as a route for synthesis of Ag NPs.

2. Experimental

2.1. Materials

N-vinylpyrrolidone (VP), supplied by MERCK-Schuchardt, was used. κ-carrageenan (KC), supplied by Acros Organics, was used. Ammonium persulphate (APS), hydroquinone, and silver nitrate were laboratory grade chemicals.

2.2. Methods

2.2.1. Preparation of poly (N-vinyl-2-pyrrolidone)/ kappa-carrageenan (PVP/KC) hybrid

The polymerization of VP in presence of KC was achieved under atmospheric oxygen in 30 ml polypropylene beaker at a specific liquor-to-KC ratio (LR) as follows: A known concentration of ammonium persulphate aqueous solution was added to a beaker containing thermostatic mixture of VP aqueous solution and KC, that are at specific liquor to material and molar ratios to each other, with continuous stirring to form a uniform paste. The beaker was then kept in a thermostatic water bath for a period of time followed by cooling the sample at ambient conditions, addition of 500 ppm of hydroquinone and finally subjected to chemical analysis.

2.2.2. Purification of a prepared hybrid for IR analysis

After completion of the polymerization reaction at its optimum conditions, the prepared PVP/KC hybrid was poured into a beaker containing 300 ml of acetone. The product was then stirred, filtered and dried at 60 ^{O}C for 48 h. The dried product after that was treated with trichloromethane in a Soxhlet apparatus for 72 h to remove PVP homopolymer whereas the PVP-g-KC was dried and stored over $CaCl_2$ in a desiccator for 48 h for IR analysis. The grafting ratio(%G) was calculated according to Fanta's equation as follows (Fanta, 1973):

$$\%G = \text{Grafted polymer}/\text{Weight of substrate} \times 100$$

2.2.3. Utilization of PVP/ KC hybrid for preparation of Ag NPs

Silver nanoparticles were prepared using silver nitrate as a precursor using the prepared PVP/ KC hybridas follows: After completion a polymerization reaction containing 0.2 g of KC and VP of a molar ratio 50% to KC, 50 ml aqueous solution containing 1 mmole $AgNO_3$ as a precursor was added to the reaction medium, without adding hydroquinone, followed by adjusting its pH at 7 and leaving it at 70 ^{O}C with stirring for 2 h. After that, the suspension was centrifuged for 15 min, The Ag nanoparticles obtained was washed with distilled water and dried at 40 °C under vacuum overnight to obtain the Ag NPs.

2.3. Testing and analysis

- The extent of polymerization, expressed as percentage total conversion, % TC, was determined by assessing the unsaturation (double bonds) content before and after polymerization (Abou-Okeil, Amr, & Abdel-Mohdy, 2012).
- Infra-Red (FTIR) spectroscopy was carried out using Bruker IR Spectrometer.
- The formation of Ag NPs was confirmed by ultraviolet-visible (UV–vis) spectroscopy using T80 spectrophotometer.
- The morphology of the synthesized Ag NPS was obtained by transmission electron microscope (TEM) using a JEOL, JEM 2100 F electron microscope at 200 kV.

3. Results and discussion

3.1. Tentative mechanism of PVP/KC hybrid formation

It was reported that graft copolymerization of vinyl monomers onto biopolymers is a promising technique to add potential application for these biopolymers by giving them desirable properties (Thakur, Thakur, & Gupta, 2013). Thus, VP was undergoing radical polymerization in presence of KC as a biopolymer and ammonium persulfate (APS) as an initiator. In aqueous medium, APS decomposes to form $SO4^{-}\cdot$ and HO· free radical species (R·) that can initiate radical polymerization reaction as shown in the following equations (Fahmy, Aly, & Sayed, 2017; Hebeish, Fahmy, Abo-Shosha, & Ibrahim, 2006; Ibrahim, Hebeish, Fahmy, & Abo-Shosha, 2006; Ibrahim, Abo-Shosha, Fahmy, El-Sayed, & Hebeish, 2008; Ibrahim, Amr, Eid, Mohamed, & Fahmy, 2012):

$$R\cdot + VP \rightarrow VP\cdot + RH \tag{1}$$

$$VP\cdot + n\ VP \rightarrow PVP\ (\text{PVP homopolymer}) \tag{2}$$

$$KC\text{-}OH + R\cdot \rightarrow KC\text{-}O\cdot\ (\text{KC macroradicals}) + RH \tag{3}$$

$$KC\text{-}O\cdot + nVP \rightarrow PVP\text{-}g\text{-}KC\ (\text{PVP grafted KC}) \tag{4}$$

Where R· is free persulphate free radical, VP· is vinyl pyrrolidone monomer free radical, KC-OH is carrageenan

The end product of the above polymerization reaction is a mixture of PVP grafted KC, PVP homopolymer as well as ungrafted KC (intact and oxidized) in a state of entanglement with each other (Fahmy et al., 2017; Hebeish et al., 2006; Ibrahim et al., 2006, 2008; Ibrahim et al., 2012). For convenience, this mixture was referred as PVP/KC hybrid. Factors affecting the polymerization reaction such as ammonium persulphate concentration, reaction temperature and time, liquor to KC ratio (LR) and KC to VP molar ratio were studied. Given below are the results with appropriate discussion.

3.2. Factors affecting preparation of PVP/KC hybrid

3.2.1. Ammonium persulphate concentration

Fig. 1 illustrates the impact of APS concentration on the extent of polymerization of VP monomers in presence of CK expressed as percent total conversion (%TC). It is obvious that increasing APS concentration from 0.0053 to 0.0105 mol/l results in a gradual enhancement in % TC indicating a generation of free radical species that enhance the initiation as well as propagation of the polymerization reaction (El-Sayed, Fahmy, Ibrahim, & Abo-Shosha, 2004; Fahmy et al., 2017; Hebeish et al., 2006).Further increasing of APS concentration, i.e. beyond 0.0105 and up to 0.0132 mol/l, does not affect % TC suggesting a presence of aplenty of free radicals that gives rise to a faster rate of termination (El-Sayed et al., 2004; Fahmy et al., 2017)

3.2.2. Liquor-to-KC ratio (LR)

Fig. 2 reveals the effect of altering LR on the extent of %TC of VP monomers in the polymerization reaction medium. It was clear that