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Development of bio-based polymeric hydrogel: Green, sustainable and low cost plant fertilizer packaging material

Saber Ibrahim[a], Galal A.M. Nawwar[b], Maha Sultan[a,*]

[a] Packaging materials department, National Research Centre, Elbehoth Street 33, 12311 Dokki, Cairo, Egypt
[b] Green chemistry department, National Research Centre, Elbehoth Street 33, 12311 Dokki, Cairo, Egypt

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ABSTRACT

Low cost green fertilizer hydrogel packaging material was prepared based on waste chicken gelatin (WCG) using peroxy grafting copolymerization technique. Gelatin was grafted with acrylamide (AM) using ammonium persulphate (APS) as initiator. The effect of acrylamide concentration on grafting efficiency was studied. Highest grafting percentage of waste chicken gelatin (WCG-g-PAm) copolymers was detected at monomer ratio (Am 2:1 WCG). The non-protein nitrogen content, FT-IR, X-rays diffraction, and scanning electron microscope were determined as an evidence of grafting process. The swelling ratios, loading efficiency of urea on WCG-g-PAm copolymers in aqueous medium, and its slow release behavior were studied and quantized by spectroscopic methods. The solvent diffusion and behavior mechanism were studied. The results revealed that swelling and release behavior follow Fickian mechanism. Thermal analysis of WCG-g-PAm copolymers was applied to exhibit evidence on the grafting process. The thermal stability and total activation energies enhanced with increasing grafting degrees of WCG-g-PAm copolymers.

1. Introduction

Various types of delivery supplies were used to provide plant with nutrients at a controlled rate and the use of hydrophilic polymers as carriers of plant nutrients is one of the widely used trends. These polymers include natural polymers derived from polysaccharides, semi-synthetic polymers and synthetic polymers which via diverse degrees of cross-linking, anionic charge, and cationic charge changing their efficiency as fertilizer carriers. Addition of some polymers with nutrients has been shown to reduce N and K leaching from well-drained soils and to increase the plant recovery of added N, P, Fe, and Mn in some circumstances [1]. Plant nutrients losses from soil are main ingredient of diffuse ground water pollution. Economically, costs of diffuse water pollution from soil can include environmental and ecosystem damage, lost aquaculture and fisheries income, and increased treatment costs for drinking water. 57% of the nitrogen (N) and 69% of the phosphorus (P) entering watercourses were from agriculture [2]. A variety of environmental and economic disadvantages associated with the application of conventional fertilizers became a focus of worldwide concern. Economically, the application of superabsorbent composite hydrogel based on cheap resources, has confirmed many advantages over the conventional types as diminishing the consumption of agriculture costs, reducing irrigation costs and frequency. Thus this technology can be applied in industry as large scale. Furthermore, the agro-chemicals demands of the plant can be met more closely by designing proper controlled release system based on biodegradable natural polymer wastes to increase efficiency and reducing the risk of overdosing the plant [3].

New fertilizers packaging technologies known as controlled-release are emerging that added further functionality and diminish cost to make slow release fertilizers. This technology can improve water retention to increase drought resistance, and reducing the amount of fertilizer required to give greatest crop yields [4].

Shaviv and Mikkelsen [5], proposed that slow-release fertilizers can be generally classified into 4 types: (i) inorganic materials of low solubility, such as metal ammonium phosphates; (ii) chemically or biologically degradable low solubility materials, such as urea-formaldehyde; (iii) relatively soluble materials that gradually decompose in soil; and (iv) water soluble fertilizers controlled by physical barrier, such as coated fertilizers. Coated fertilizers, physically prepared by coating fertilizer granules with

* Corresponding author. Fax: +20 233322918.
E-mail addresses: Saberam2000@yahoo.com (S. Ibrahim), gnawwar@yahoo.com (G.A.M. Nawwar), mahasultan21@yahoo.com (M. Sultan).

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various materials, are the major categories of the slow-release fertilizers. Many materials have been reported as coatings, such as polysulfone, polyvinyl chloride, and polystyrene [6,7].

Superabsorbent polymers are three-dimensional network materials which, present as in a gel status which may absorb ≥500% of water by weight. Recently, researchers on the use of superabsorbent composites as water and fertilizers carriers pay a great attention. Results observation as showed reducion in irrigation water consumption, improvement in fertilizers retention in soil, lowering the death rate of plants, and promoting plant's growth [8]. Free radical vinyl graft copolymerization onto natural polymers is a well-known method for synthesis of natural-based superabsorbent hydrogels [9]. The monomers, acrylamide (AM) and acrylic acid (AcA) were easily graft copolymerized onto gelatin backbone [10]. Novel eco-friendly superabsorbent composite of flax yarn waste-g-poly (acrylic-co-acrylamide) was prepared by free radical graft copolymerization. The optimal synthesis conditions of initiator concentration, acrylamide/acrylic acid ratio to cellulose mass ratio, reaction time and, temperatures were studied. The attained product had the best water absorbency of 875 g/g in distilled water [8].

Among available wastes, gelatin and collagen usually are extracted from the skin of domestic mammals, such as pigs, calves and cows [11]. Recently, recycling of gelatin scraps was reported along with the synthesis of gelatin composites incorporating 2-methyl-4-chlorophenoxy acetic acid (MCPA) to be used as herbicide and the prepared formulation proved to be useful for agricultural applications [12]. Synthesis of gelatin-graft-poly (sodium acrylate-co-acrylamide) superabsorbent hydrogels with salt and pH-responsiveness properties was reported and the swelling behavior of these absorbent polymers in saline solution and solutions with different pH was also investigated [13]. Cationic gelatin graft copolymer was also developed by the graft copolymerization reaction of gelatin with acrylamide (AM) and methacryloyloxyethyl trimethyl ammonium chloride (DMC) [14].

According to our local waste treatments, related to the exploitation project of wastes to be transformed into valuable products in Egypt [15,16]. Our attention was directed towards providing superabsorbent hydrogels packaging material as fertilizer carrier by management of grilled waste gelatin. However, there are no reports which focus on the application of grilled waste gelatin in this scope. Thus, this work aimed to develop slow release fertilizer packaging material to overcome fertilizer high cost and environmental pollution in soil and ground water. In order to satisfy the requirements of low production cost and environmental safety, we developed sustainable root-targeted delivery fertilizers packaging material system from food waste processing (grilled waste gelatin). This root-targeted delivery packaging polymer was prepared by peroxy copolymerization of acrylamide monomer onto grilled chicken protein residue (gelatin-collagen waste). The attained target delivery system was characterized and its swelling and release profile were investigated.

2. Experimental

2.1. Materials

Chicken gelatin waste was obtained from grilled chicken proteinous residue that was collected from different restaurants in Cairo province, Egypt. Acrylamide was obtained from (Alpha Chemical Bumbai, India). Ammonium persulfate (Aldrich, Germany), Methylene bisacrylamide (Aldrich, Germany), 2-acrylamido-2-methylpropanesulfonic acid (ACROS, Belgium) were used without further purification. Methanol, ethanol, isopropanol, and the other solvents were used as received.

2.2. Isolation and purification of waste chicken gelatin (WCG)

One kilogram of released liquid waste from chicken during grilling process was obtained. The liquid was held at low temperature (0 °C) for 6 h for solidification and the top fat layer was skimmed. The remaining was thawed then filtered by using cheese cloth for separation of any foreign matters and evaporated to dryness at reduced pressure (50 °C, 0.6 mbar). The obtained residue was extracted with hexane to be free of fats and then, the obtained defatted gelatin waste was ready for grafting process.

2.3. Synthesis of waste chicken gelatin-g-polyacrylamide (WCG-g–PAm)

WCG-g-PAm copolymers were synthesized by grafting varying acrylamide concentrations and constant WCG concentrations via peroxy grafting copolymerization technique using ammonium persulphate (APS) initiator. Three different grafted copolymer formulations in which waste chicken gelatin (WCG) to acrylamide (AM) weight ratios typed as Wg_1 (1:1), Wg_2 (1:2), and Wg_3 (1:3). The typical details of grafting procedure are given below:

Defined pre-weighed of extracted waste chicken gelatin (4.0 g) was dissolved in 40 mL of Millipore water (distilled water with electrical resistance of 18.2 MΩ cm at 25 °C) and filtered to remove its insoluble salt. The solution was added to a 500 mL 3-neck double jacket flask equipped with a mechanical stirrer (Cafram BDC 2002, Canada) and the flask was thermostatic temperature at (80 °C). Then 2-acrylamido-2-methylpropanesulfonic acid (3.0 g) was added to the reactor. After stirring for 10 min, ammonium persulfate (0.20 g of APS in 5 mL of H_2O) and methylene bisacrylamide (0.10 g in 5 mL of H_2O) were added simultaneously to the reaction mixture. The temperature was maintained at 80 °C and the reaction mixture was stirred continuously (300 rpm) for 1 h. At the end of the propagation reaction, the gel product was poured into ethanol (200 mL) and was dewatered for 12 h. Then the product was cut into small pieces, washed with 200 mL of ethanol, and filtered. The particles were dried in an oven at 50 °C over night. After being ground, the powdered superabsorbent hydrogel was stored in the absence of moisture, heat, and light.

2.4. Characterization

2.4.1. Nitrogen content

The true protein nitrogen and non-protein nitrogen contents (NPN) of WCG-g-PAm copolymers were determined as described in Association of Official Analytical Chemists standard technique (AOAC) by Waldo and Goering [17]. Non-protein nitrogen contents were calculated by subtracting the true protein nitrogen content value from total nitrogen content values.

2.4.2. FT-IR

The obtained sample was ground into small particles and dried in vacuum at 50 °C for 24 h. The dried samples were analyzed in KBr discs by FT-IR (JASCO FT/IR-4100, Japan).

2.4.3. X-ray diffraction pattern

X-ray diffraction patterns were obtained by using PAN analytical XPERTPR O Super X-ray diffractometer equipped with Co Kα. The tube operated at 45 kV, 9 mA.

2.4.4. Scanning electron microscope (SEM)

The scanning electron microscope using SEM Model Quanta 250 FEG (Field Emission Gun) attached with EDX Unit (Energy Dispersive X-ray Analyses), with accelerating voltage 30 kV, magnification 14 xs up to 1,000,000 and resolution for Gun.1n.