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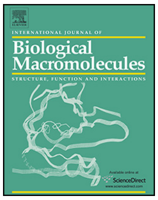

Electrically conducting silver/guar gum/poly(acrylic acid) nanocomposite

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ABSTRACT

This article describes the synthesis of an electrically conducting silver/guar gum/poly(acrylic acid) nanocomposite hydrogel. The synthesis process started with grafting acrylic acid monomers onto the natural polymer guar gum by the use of ammonium persulphate as a free radical initiator in acid medium. Guar gum/poly(acrylic acid) graft copolymer was separated from the polymerization medium, purified and subjected to crosslinking treatment, using alkaline epichlorohydrin as a crosslinking agent. Silver nitrate solution was added during the crosslinking treatment in varying concentrations, that the reaction conditions affect crosslinking of guar gum/poly(acrylic acid) graft copolymer to a hydrogel, as well as reduction of silver nitrate to silver nanoparticles, giving rise to the formation of silver/guar gum/poly(acrylic acid) nanocomposite. Factors affecting the grafting reaction as well as those affecting the crosslinking/reduction treatment were optimized. The so synthesized nanocomposite hydrogel samples were fully characterized, regarding their contents of silver nanoparticles and swelling ratio. The electrical conductivity of the nanocomposite hydrogel was studied and it was found to be affected by the swelling ratio of the hydrogel as well as its content of silver nanoparticles.

1. Introduction

A considerable interest in hydrogels has been created in the scientific research media due to their unique properties and variable applications. Hydrogels are novel materials which have many promising applications in various technological fields like pharmaceutical and biomedical applications, tissue engineering applications and many other environmental technologies [1–6]. The most simple and common definition of hydrogel states that the term hydrogel represents a three-dimensional network structure of a hydrophilic polymeric material, which upon direct contact with solutions, they are capable of absorbing large amounts of this solution, swollen and retain the solution inside this network structure [7,8].

In order for a hydrogel to be conductive, its polymeric structure must combine a hydrogel structure with superior water absorption properties and includes in its structure another conductive material, like conductive polymers or metals. The conductivity characteristics of such conducting hydrogel will be heavily dependent on both the structure and concentration of the conducting polymer or metallic component within the whole hydrogel structure. One of the most common approaches to prepare such conducting hydrogels is to polymerize some kinds of conducting polymers or to incorporate a metallic conductor inside the structure of the hydrogel matrix [9,10].

When metals are converted from the bulky particle size scale to the nanoparticle size scale, these metals exhibit completely different properties. Such change in definite metal properties, like electronic properties, chemical properties and spectroscopic properties for the same metal, when converted from the bulky size scale to the nanosize scale is attributed to the decrease in size which accordingly results in large increase in the metal surface area in the nanoscale. So the materials when converted to the nanosize scale will have a smaller size and accordingly larger surface area and these characters will create applications for these metals in a wide variety of technological fields [11–23].

Many researchers reported different routes for synthesizing different metallic nanoparticles in different preparation protocols. These preparation protocols include a synthetic route by means of metal salts reduction [24–29], autoclave synthesis route, in absence of any reducing agent [30,31], reverse micelles synthesis route [32,33], synthetic route via electrochemical reaction [34,35] and synthetic route via different irradiation techniques [36,37].

Many technical products are synthesized by grafting different synthetic polymers onto different biological polymers. These technical compounds resulting from this grafting process, which have

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wide range of technical applications are said to be graft copolymers. One of the most important advantages of this route of chemical synthesis is that they produce completely new functional molecules. These novel functional products combine the desired technical properties of both graft copolymer components, those of synthetic polymer and those of biological polymer. This route of chemical modification has become a very important way for synthesizing novel and advanced products, via introducing new functional properties into the structure of biological polymers [38,39]. Conventional initiation methods for graft copolymers synthesis involve redox initiation techniques [40–43], microwave-assisted initiation [44,45], γ-ray irradiation initiation technique of grafting [46–48], electron beam initiation technique of grafting [49,50] and many other miscellaneous initiation techniques for grafting [51,52].

Many industrial applications like lithium batteries, solar cells, capacitors, and fuel cells are based on technical conducting hydrogels [53,54]. On the other hand, nanocomposites composed of nanometal particles dispersed in a polymer attracted considerable attention in the recent years and many researchers have interest in the so-called hydrogel-nanometal nanocomposites [55]. These hydrogel nanocomposite find wide range of applications in technical fields like memory devices, artificial muscles, photographic materials, switches and catalysts [56]. Silver nanoparticle is known to be easy to reduce and when subjected to the visible region of the UV light, they exhibit strong surface plasmon resonance with high energy. In dielectric field, metal nanoparticles can overcome the attraction forces and stabilize themselves from aggregation, that is why the synthesis of hydrogel nanocomposites containing metal nanoparticles is very promising approach to prepare novel materials which can exhibit desired properties arising from its constituents, namely the nanoparticles and polymeric hydrogel matrix and in this regard several methods for the preparation of metal–polymer nanocomposites were reported [57–60].

The present work aims at the preparation of silver/guar gum/polyacrylic acid nanocomposite hydrogel, through grafting acrylic acid onto guar gum and then subjecting the graft copolymer to epichlorohydrin treatment in presence of silver nitrate in alkaline medium, where these conditions affect crosslinking of the graft copolymer into hydrogel and conversion of silver ions to silver nanoparticles.

2. Experimental

2.1. Materials

High molecular weight guar gum (GG) (MW 70,000), acrylic acid (AA), ammonium persulphate, epichlorohydrin, sodium hydroxide, silver nitrate and sulphuric acid were all laboratory grade reagents.

2.2. Grafting acrylic acid onto guar gum

Guar gum (5 g) is stirred in 50 mL of water and after complete dissolution; the pH is adjusted at 2–2.5 by use of diluted sulfuric acid. The solution is kept under continuous stirring and acrylic acid (50–200% on weight of guar gum) is added to the dissolved guar gum. The mixture temperature is raised to 60 °C, keeping continuous stirring. At the desired reaction temperature, 3% from ammonium persulphate (based on the weight of acrylic acid) is added and the graft copolymerization reaction is left running. The polymerization reaction results in the formation of polyacrylic acid/guar gum graft copolymer as well as the homopolymer polyacrylic acid. The progress of the polymerization reaction is monitored by measuring the percentage total conversion of the monomer acrylic acid to polyacrylic acid, either homopolymerized or grafted onto the guar gum. The total conversion was measured quantitatively by estimating the acrylic acid double bonds throughout the reaction period and it was found that 100% total conversion is attained in a duration of maximum 120 min. The graft copolymer is separated from the homopolymer by precipitating the former from the polymers blend using the non-solvent ethyl alcohol. The precipitated graft copolymer is filtered, washed several times with alcohol, dried in an air oven at 50 °C overnight, ground well to fine powder and its graft yield is measured gravimetrically using the mathematical formula (1):

$$\%\text{G.Y.} = \frac{W_2 - W_1}{W_1} \times 100 \qquad (1)$$

where W_1 is the dry weight of guar gum sample incorporated in the polymerization reaction and W_2 is the dry weight of the produced graft copolymer.

The synthesis of guar gum/poly(acrylic acid) graft copolymer is represented in Scheme 1.

2.3. Simultaneous crosslinking/synthesis of silver/polyacrylic acid/guar gum nanocomposite hydrogel

Finely grinded guar gum/poly(acrylic acid) graft copolymer (10 g) was dissolved in 100 mL of 0.1 N sodium hydroxide aqueous solution. Mechanical stirring is continued until complete dissolution of the graft copolymer in the aqueous alkaline solution is achieved. Different concentrations from epichlorohydrin, 2–8% (based on weight of graft copolymer) and 0.1 N silver nitrate (0–10 mL) are added drop wise to the graft copolymer solution, keeping the stirring continuous and vigorous. The stirring continuous for 15 min after the end of epichlorohydrin and silver nitrate addition and at this end, the formed paste is removed from the reaction medium, dried for 2 h at 80 °C in an air oven, then cured at temperatures ranging from 120 °C to 180 °C for 2 min [61]. The abovementioned process leads to affecting crosslinking of guar gum/poly(acrylic acid) graft copolymer to hydrogel through the crosslinking agent epichlorohydrin, as well as affecting the reduction of silver ions to silver nanoparticles through the reduction effect of the graft copolymer's functional groups in such alkaline medium. These silver nanoparticles will be distributed inside the hydrogel structure forming what is known as silver/guar gum/poly(acrylic acid) nanocomposite. The crosslinking of guar gum/poly(acrylic acid) graft copolymer to hydrogel is represented in Scheme 2.

2.4. Testing and analysis

2.4.1. Swelling behavior

Traditional gravimetric procedure was used as a simple technique to assess the swelling capacity of the prepared silver/guar gum/poly(acrylic acid) nanocomposite hydrogel. Hydrogel samples are weighed accurately (on dry basis) and immersed for about 24 h in distilled water at room temperature and this duration is enough for the hydrogel sample to swell as much as possible or to reach its maximum swelling capacity. The hydrogel samples after complete swelling are removed from the immersion bath and wiped carefully and gently with filter paper without applying any pressure on them in order just to remove the excess water from their surfaces but not squeeze them to get the absorbed water inside their structures. The swollen samples are then weighed accurately to assess the swelling ratio (SR) according to the mathematical formula (2):

$$\text{SR} = \frac{W_s}{W_d} \qquad (2)$$

where W_d is the dried sample weight (g) and W_s is the swollen sample weight (g).