Carbohydrate Polymers 91 (2013) 693–698

Contents lists available at SciVerse ScienceDirect

Carbohydrate Polymers

journal homepage: www.elsevier.com/locate/carbpol

An innovative method for preparation of nanometal hydroxide superabsorbent hydrogel

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ARTICLE INFO

Article history:
Received 2 June 2012
Received in revised form 6 August 2012
Accepted 17 August 2012
Available online 4 September 2012

Keywords:
Hydrogel
Acrylic acid/acrylate
Electro-deposition
Conductivity

ABSTRACT

A novel method for preparation of a conducting nanometal hydroxide hydrogel was undertaken. In situ accommodation of metal hydroxide nanoparticles within swollen hydrogel networks is developed. Thus, poly(acrylic acid/acrylate) hydrogel (PAAc/AC) was prepared by simultaneous polymerization of acrylic acid/acrylate (AAc/AC). Electrodeposition hydroxide of nanoiron and nanocopper into (PAAc/AC) hydrogel was performed. Swelling behaviour and swelling kinetics of prepared hydrogel were evaluated in media having different pH values. The conductivity of both PAAc/AC/nanocopper hydroxide and PAAc/AC/nanoiron hydroxide were measured in comparison with that for PAAc/AC hydrogel. An amelioration in conductance of PAAc/AC hydrogel having 0.8×10^3 μS after being incorporated with nanocopper hydroxide and nanoiron hydroxide to be 1.5×10^3 μS and 2.6×10^3 μS, respectively has been achieved. Distribution of the metal hydroxide nanoparticles penetrated within the hydrogel networks using transmission electron microscopy has been thoroughly elucidated.

1. Introduction

Superabsorbent polymers are characterized by a network structure with a suitable degree of crosslinking. They can absorb and retain huge amounts of water or aqueous solutions and are capable of absorbing hundreds to thousand times its own mass of water to form a stable hydrogel; however retained water is also hardly to be removed under some pressure (Lee & Chen, 2005). They are currently used in many areas of application including hygienic products (Singh, Sharma, Garg, & Garg, 2010), agriculture (Saxena, 2010), drug delivery systems (Singh et al., 2010), sealing (Singh et al., 2010), coal dewatering (Sun, Zhang, Shi, Tang, & Wu, 2002), and artificial snow (Singh et al., 2010), food additives (Chen et al., 1995), pharmaceuticals (Kashyap, Kumar, & Kumar, 2005), biomedical applications (Anton, 1990) tissue engineering and regenerative medicines (Ling Zhang et al., 2011), diagnostics (Van der Linden, Herber, Olthuis, & Bergveld, 2003), wound dressing (Sikareepaisan, Ruktanonchai, & Supaphol, 2011), separation of biomolecules or cells (Feng Wang et al., 2010) and barrier materials to regulate biological adhesions (Roy, Jennifer, & Brent, 2010), Biosensor (Peter Krsko et al., 2009).

Recently, many researchers pay much attention on the superabsorbent polymer for developing new applications, such as conducting materials, biomaterials, sensors, release matters and wave-absorbing materials (Qunwei Tang et al., 2008). However, researches on conducting polymer (or hydrogel) based on the superabsorbent polymer are rather few. A conducting hydrogel could be used in fuel cells, supercapacitor, dye sensitive solar cell and rechargeable lithium batteries (Lan et al., 2006; Lewandowski, Zajder, Frackowiak, & Beguin, 2001; Pissis and Kyritsis, 1997; Tang et al., 2008) due to a number of reasons including better conductivity character, colloid stability, low cost and simple preparation.

Since few decades, there has been a great deal of interest in biocomposites containing metal oxide nanoparticles dispersed in polymeric, glassy or ceramic matrices. Iron oxide nanoparticles display a great scientific interest in technological applications such as high density magnetic recording media (Cornell & Schwertmann, 2003), biosensors (Perez, Simeone, Saechi, Josephson, & Weissleder, 2003), ferrofluids (Anton, 1990), magnetic resonance imaging (Oswald, Clement, Chambon, Claeys, & Frija, 1997) and biomedicine (Fu, Dravid, & Jhonson, 2001).

Recently, detailed studies have been carried out on nanocomposites to gain advantages of their unique properties, and conducting polymer–metal nanocomposites will be typical of these kinds (Gaddy & McLain, 2004). Actually, there are many polymer/nanoparticle composite materials, and optimal control over the structure of the composite could be achieved by preassembling

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http://dx.doi.org/10.1016/j.carbpol.2012.08.056

the inorganic nanoparticles with the organic polymer matrix (Wei, Luo, Zhang, Fan, & Chen, 2008).

Progressive research has been carried out to synthesize various types of metal nanoparticles using different ways of preparation. These ways include sputtering, laser ablation, inert gas condensation, oven evaporation, spray conversion pyrolysis, flame hydrolysis, deposition, high energy milling, sol–gel deposition, and electrodeposition (Wei et al., 2008).

Traditionally, such a synthesis is carried out chemically making use of a reducing agent such as sodium borohydride or with irradiation to convert groups of metal ions into nanoparticles (Wei et al., 2008). Pileni et al. reported the synthesis of copper nanoparticles of varied shapes by using reverse micelles as micro-reactors and protecting shells (Pileni, Krzywicki, Tanori, Filankembo, & Dedieu, 1998). Gedanken and coworkers reported that excellent surface resonance can be observed for copper nanoparticles when prepared by a sonochemical technique (Dhas, Raj, & Gedanken, 1998).

Nanosized copper grains as conductive particles has a number of advantages over traditional copper conductive particles, for example, high surface activity, good electro-conductivity and heat-conductivity, ease of fabrication, as well as other nanosized effects (Fan, Zhang, Zhan, & Wu, 2006). They have found wide applications in mechanics, magnetics, electrical and chemical aspects.

It has been reported by Cioffi et al. for the first time the possibility of using copper/polymer nanocomposites as a bioactive coating against fungi (Cioffi & Torsi, 2005). However, examples dealing with copper/polymer composites as conductive composites for chemical vapour or gas sensors are very rare. Since agglomeration and oxidization are still two main disadvantages as nanoscale copper conductive particles, investigations into their preparation, fabrication and applications attracted much attention.

Conducting hydrogel is a novel functional material that has been developed recently. It is possible to be employed as conducting film, coating, sensor, conducting fiber, wave absorbing material and other applications (Ali, 2006; Li, Guo, Wei, Mac Diarmid, & Lelkes, 2006). The conducting hydrogel often was prepared by copolymerizing or doing conducting materials with/to hydrophilic monomers/polymers (Aouada et al., 2006).

Polymer hydrogel electrolyte was successfully prepared via high ionic conductivity close to that of 1 M H_2SO_4 aqueous solution (Wada et al., 2006). The high ionic/protonic conductivity of hydrogel is of prime importance in some applications as exemplified by cells and sensors.

The present work is based on a superabsorbent polymer polyacrylate, a scheme for developing a novel and simple method for preparation of a conducting nanometal hydroxide hydrogel is planned. In situ preparation of metal hydroxide nanoparticles within swollen hydrogel networks is undertaken. Thus, poly (acrylic acid/acrylate) hydrogel (PAAc/AC) was obtained. Electro deposition of nanoiron hydroxide and nanocopper hydroxide into superabsorbent hydrogel were investigated. Swelling behaviour and swelling kinetics of the so obtained hydrogels were evaluated. The conductivity of both PAAc/AC/nanoiron hydroxide and PAAc/AC/nanocopper hydroxide were measured and compared with that of PAAc/AC. Distribution of the metal hydroxide nanoparticles within the hydrogels using transmission electron microscopy (TEM) was thoroughly investigated.

2. Materials and methods

2.1. Materials

Acrylic acid (AAc) in the monomeric form was produced by Sisco Research Lab. Pvt. Ltd., India. N,N′-methylenebisacrylamide (MBA) as a crosslinking agent, potassium persulphate (KPS) as initiator and potassium hydroxide (KOH) were supplied by Sigma–Aldrich, Inc. These reagents were used as laboratory grade chemicals.

2.2. Preparation of polyacrylate superabsorbent polymer

Preparation of polyacrylate superabsorbent polymer was carried out according to a modified procedure (Wu, Zhong, Lin, Wei, & Xie, 2006). A mixed solution of acrylic acid monomer and potassium acrylate was prepared by agitating the monomer with (N,N′-methylene bisacrylamide) as a crosslinker in presence of potassium hydroxide in distilled water under ambient conditions. Under a nitrogen atmosphere, the mixture solution was stirred and heated to 80 °C in a water bath for 15 min., followed by addition of the initiator. The reaction mixture was kept under stirring for few minutes to complete polymerization reaction.

2.3. Electro-deposition of nanometal hydroxides into superabsorbent hydrogel

The electro-deposition was carried out using two electrodes system, where iron or copper was fixed as anodes and graphite plate as cathode into a glass cell 15 cm × 7.5 cm × 8 cm using a Power Supply (GW Lab DC GPR-3030).

A known weight of the swollen superabsorbent hydrogel was prepared and filled into the cell between two electrodes. It has been considered that the distance between the electrodes was kept constant throughout the experiments of using different types of iron and copper anodes. The anodic dissolution of iron and copper was carried out at room temperature and duration of 15 min, while electric potential varied to study the amount of metal ion dissolved. Conductivity meter (D8120 Weilhein WTW LF-6) was employed to measure the conductance of swollen superabsorbent hydrogel before and after the anodic dissolution of iron and copper into the eletrolytic cell.

2.4. Measurements and characterization

2.4.1. Transmission electron microscopy (TEM)

TEM images for the prepared superabsorbent hydrogel and nanometal hydrogel composites were recorded by a JEOL JEM-1230 electron microscope operating at an acceleration voltage of 100 kV. Specimens for TEM were prepared by placement of a swollen sample of superabsorbent hydrogel on a 400-mesh copper grid and the evaporation of excess water in air at room temperature.

2.4.2. Swelling studies

The swelling characteristics of the prepared hydrogel were measured via gravimetric analysis (Li et al., 2006). The swelling ratio is the criterion of describing water absorption capacity. Measurement of the swelling ratio of the prepared hydrogel was conducted by the so-called tea-bag method (Zhao, Kang & Tan, 2006), and using distilled water as liquid to be absorbed. The bags used were made of nonwoven polypropylene. The dried samples confined in nonwoven polypropylene bags were placed in different swelling media with different pH values under ambient conditions and taken from swelling media at regular periods of time. The surface water on the swollen hydrogel was removed by soft pressing the bag sample between the folds of a filter paper; an increase in weight was determined.

The equilibrium swelling of the gels was determined as follows: gels were dried for 3 days at room temperature and were then dried under vacuum at 80 °C. After the weight of the dried samples was determined, the samples were equilibrated in swelling media for a day at room temperature and then weighed again. The