Available online at www.sciencedirect.com
ScienceDirect
Reactive & Functional Polymers 66 (2006) 1482–1493
REACTIVE & FUNCTIONAL POLYMERS
www.elsevier.com/locate/react

Semi-IPNs of starch and poly(acrylamide-co-sodium methacrylate): Preparation, swelling and diffusion characteristics evaluation

P.S. Keshava Murthy [a], Y. Murali Mohan [a,1], J. Sreeramulu [b], K. Mohana Raju [a,*]

[a] *Synthetic Polymer Laboratory,Department of Polymer Science and Technology, Sri Krishnadevaraya University, Anantapur 515 003, AP, India*
[b] *Department of Chemistry, Sri Krishnadevaraya University, Anantapur 515 003, AP, India*

Received 6 October 2005; received in revised form 20 April 2006; accepted 20 April 2006
Available online 5 June 2006

Abstract

Semi-interpenetrating polymer network (IPN) hydrogels composed of starch and random copolymer of poly(acrylamide-co-sodium methacrylate) [poly(AAm-co-NMA)] were prepared by polymerizing an aqueous solution of acrylamide (AAm), sodium methacrylate (NMA) using ammonium persulphate (APS)/*N*,*N*,*N*^{1},*N*^{1}-tetramethylethylenediamine (TMEDA) as redox initiating system in presence of a crosslinker and starch solution. IR spectroscopy was used to identify the presence of different repeating units in the IPN networks. The swelling and diffusion characteristics, such as initial swelling rate (r_i), swelling rate constant (k_s), equilibrium swelling ratio (S_{eq}), diffusion constant (n) and diffusion coefficients (D) were evaluated for different semi-IPN hydrogels prepared under various formulations. For better understanding of network structure formation of these semi-IPNs, three different crosslinkers namely, *N*,*N*-methylenebisacrylamide (MBA), 1,4-butanediol diacrylate (BDDA) and diallyl phthalate (DP) were employed. Further, the swelling pattern of semi-IPN hydrogels was studied in different physiological, pH and ionic/salt solutions and showed great responsiveness due to their ionic character. The morphological features of these IPNs were observed using scanning electron microscopy (SEM).

Keywords: Interpenetrating polymer network; Hydrogel; Superabsorbent polymer; Crosslinker; Swelling ratio

1. Introduction

Hydrogels are polymeric materials containing a large number of hydrophilic groups capable of holding large amount of water in their three-dimensional networks. They swell by absorbing water and shrink on drying [1–3]. They can hold lot of water even under pressure as well as fluid containing electrolytes. They undergo a volume phase change in response to a change in external stimuli, such as pH, ionic strength, temperature, electric filed, solvent and pressure [4–14]. All these properties of the hydrogels made them as important materials in a variety of industrial applications as well as in consumer items.

* Corresponding author. Tel.: +91 8554 255655; fax: +91 8554 255710.
E-mail address: kmrmohan@yahoo.com (K.M. Raju).
[1] Present address: Department of Material Science and Engineering, Gwangju Institute of Science and Technology, Gwangju, Republic of Korea.

1381-5148/$ - see front matter © 2006 Elsevier B.V. All rights reserved.
doi:10.1016/j.reactfunctpolym.2006.04.010

Starch is a well-known biodegradable natural polymer and is abundantly available material with low cost. Starch is used in various commercial applications due to its gelatin characteristic. Higher proportion of acrylic acid containing starch copolymers found great utility as cosmetic packs. This particular characteristic of starch made it to use as a thickener and sizing agent in textile and paper industries. Partially neutralized poly(methacrylic acid) and poly(acrylic acid) hydrogels and their copolymer hydrogels of poly(acrylamide) are most important due to their higher water absorption, retention capacity for longer time and responsiveness towards stimuli which is a required criteria to many applications and therefore many studies were reported in the literature on this aspect [15–22]. Tsuchiya et al. [16] prepared polymers of starch-g-acrylic acid along with salts of acrylic acid polymer, partially hydrolysed poly(acrylamide) and partially neutralized poly(acrylic acid) and found to have higher absorbing capacity. Starch-g-acrylic acid copolymer was employed to maintain the tomatoes for their freshness at room temperature up to 168 h as against a control sample, which showed softening at 72 h [17]. Starch-based micro hydrogel was employed on skin (surgical dressing) to maintain constant temperature [18]. Kizawa et al. [19] developed starch–acrylate copolymer, which regulates the pH (6.7) and showed higher water holding capacity when mixed with soil. Sasaki [20] patented starch-based copolymer for declogging the nozzle within ink cassettes of ink-jet printers. It is possible to control dust raising, prevent water evaporation and reduce the total cost of truck transportation by spraying the emulsion of a superabsorbent resin based on acrylic acid and starch on the floor of tar liquid on road-way [21,22].

Most of the above applications depend on absorption characteristics of the hydrogels. Recently, we studied IPN hydrogels composed of polyvinyl alcohol (PVA) with poly(acrylamide-co-sodium methacrylate) and poly(acrylamide-co-potassium methacrylate) in responsive to temperature, pH, salt and biological fluids [23,24]. The reaction parameters such as monomer concentration, type of crosslinker and concentration of crosslinker, initiator and activator have a great impact on the swelling capacity of the IPNs. The morphology of the IPN hydrogels also supports the swelling variations.

In the present era, increasing of garbage mountains is looked as an ecological threat. At this movement, the use of biodegradable starch in consumer items along with acrylamide/acrylic acid/methacrylic acid copolymers will be an interesting study. Therefore, we are interested in studying of IPN hydrogels based on starch and poly(acrylamide-co-sodium methacrylate). In the present investigation, semi-IPN hydrogels of starch with random copolymer poly(acrylamide-co-sodium methacrylate) were prepared and also studied in detail their swelling and diffusion characteristics by changing various reaction parameters as well as their response to external stimuli such as pH, different salt solutions, biological fluids, etc. on the swelling capacity of IPN hydrogels. The present work also describes the morphological changes (crosslinking networks) affecting the swelling behaviour of semi-IPN hydrogels.

2. Experimental

2.1. Materials

Acrylamide (AAm), ammonium persulphate (APS), soluble starch (ST) and N,N^1-methylene-bis-acrylamide (MBA) were purchased form S.D. Fine-Chem Ltd., Mumbai. Methacrylic acid, 1,4-butanediol diacrylate (BDDA), diallyl phthalate (DP) and N,N,N^1,N^1-tetramethylethylenediamine (TMEDA) were obtained form Aldrich Chemical Company Inc. (Milwaukee, WI, USA). All the chemicals and reagents were used as received. Double distilled water was used for polymerizations and swelling experiments. Sodium methacrylate (NMA) was prepared by neutralization of methacrylic acid with sodium hydroxide.

Stock solutions of MBA (1 g/100 ml dist. water), BDDA (1 g/100 ml methanol), DP (1 g/100 ml methanol), APS (5 g/100 ml dist. water) and TMEDA (1 g/100 ml dist. water) were prepared and used for the polymerization reactions. Different pH solutions and various physiological solutions (saline water, synthetic urine, urea and D-glucose) were prepared [23,24].

2.2. Preparation of starch/poly(AAm-co-NMA) semi-IPN hydrogels

The semi-IPN hydrogels of starch and poly(acrylamide-co-sodium methacrylate)s were prepared by free-radical crosslinking copolymerization at normal atmospheric conditions for a period of 24 h. The preparation of IPN hydrogels was done by the method developed by Dhara et al. [25]. Different