Material Properties

Electrochemical and mechanical properties of hydrogels based on conductive poly(3,4-ethylene dioxythiophene)/poly(styrenesulfonate) and PAAm

Fauze A. Aouada a, Marcos R. Guilherme a, Gilsinei M. Campese b, Emerson M. Girootto a, Adley F. Rubira a, Edvani C. Muniz a, *

a GMPC Grupo de Materiais Poliméricos e Compósitos-DQI, Universidade Estadual de Maringá, Maringá-Paraná, Brazil
b Faculdade de Engenharia Química, Departamento Sistemas Químicos e Informática DESQ-FEQ, Universidade Estadual de Campinas, UNICAMP-Campinas-SP, Brazil

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Abstract

This paper reports on the effects of poly(3,4-ethylene dioxythiophene)/poly(styrenesulfonate) (PEDOT/PSS) entangled in the polyacrylamide (PAAm) network by the formation of a semi-IPN on hydrogel performance. Hydrogel properties were evaluated by scanning electron microscopy, water uptake, compressive load tests, ionic conductance and capacitance measurements. It has been found that the introduction of PEDOT/PSS leads to changes in the hydrogel morphology as compared to that of PAAm hydrogels. In addition, PAAm networks with good mechanical properties have been obtained. The presence of PEDOT/PSS increased the ionic conductance of swollen semi-IPN hydrogels substantially. Electrochemical experiments demonstrated that PAAm-PEDOT/PSS hydrogel is electrochemically stable and presents reversible responses to electrochemical stimuli.

Keywords: Conductive hydrogels; PAAm; PEDOT/PSS; Electrochemical properties; Mechanical properties

1. Introduction

An increasing interest in the use of polymer hydrogels in biotechnological applications has been observed in recent years [1]. This has been attributed to the fact that these materials swell in either water or biological fluids [2,3]. Appropriate electric stimuli may modify the swelling capacity of hydrogels with specific properties [4]. This affects their mechanical properties and morphology, which are parameters that correlate hydrogel behavior and its applications. For these reasons, particular consideration has been paid to polymers that respond to appropriate stimuli. Hydrogels, in conjunction with conducting polymers (CPs), form materials capable of undergoing chemical and/or physical transitions in response to appropriate electrical field stimuli [5]. It is possible to produce environmentally sensitive hydrogels, or ‘intelligent’ hydrogels, whose physical–chemical properties, such as surface topography and rheological properties, vary in response to specific environmental stimuli [6,7]. Many different hydrogels have been synthesized. Some respond to pH, temperature, pressure, stress, chemical species, ionic strength, electric field, and light [8–13]. Such ‘intelligent’ materials open the doors for novel applications in nanotechnology areas (actuators, substrates, and artificial muscles), surgical implants and tissue engineering [14] due to the unique ability...
of hydrogels to undergo phase transition under the influence of low stimuli [15]. The application of hydrogels as sensors, membranes, biomaterials [16–18], actuators [19], and in surface modification [20] requires materials with different shapes and sizes.

By using a semi-interpenetrating method, we have prepared conducting hydrogels of poly(3,4-ethylene dioxythiophene)/poly(styrenesulfonate), PEDOT/PSS, and polyacrylamide gel. The goal was to prepare hydrogels keeping their mechanical characteristics and the conductive properties of PEDOT/PSS.

2. Experimental

2.1. Materials

Acrylamide, AAm, (Aldrich), N,N’-methylene-bis-acrylamide, MBAAm, (Plusone, 17-1304-02), N,N,N’,N’-tetramethylethylenediamine, TEMED, (Aldrich, T2-250-0), Sodium persulfate, (Aldrich), and an aqueous colloidal dispersion (1.2 wt-%) of poly(3,4-ethylene dioxythiophene)/poly(styrenesulfonate), PEDOT/PSS, (trade name Baytron-P, Bayer AG, Germany) were used in hydrogel preparation. A schematic drawing of the PEDOT/PSS structure is shown in Fig. 1.

2.2. Preparation of hydrogels

Cross-linked PAAm with entangled PEDOT/PSS was obtained by the polymerization/cross-linking of acrylamide and MBAAm in aqueous solution containing PEDOT/PSS. Sodium persulfate at 4.2 mmol L\(^{-1}\) was used as an initiator. After homogenization, the solution was purged by N\(_2\) bubbling for 20 min at room temperature. Finally, TEMED at 2.85 mmol mL\(^{-1}\) in conc., used as catalytic agent, was added to the resulting solution, which was quickly placed between two glass plates (12 × 12 cm) separated by a rubber gasket (3.0 mm) and kept at room temperature. After 24 h, the hydrogels were removed from the plates in membrane form. The gels were labeled (A–M–X), where A means the molar concentration of AAm of the feed solution (in mol L\(^{-1}\)), M is the MBAAm concentration (in mol% relative to the AAm concentration), and X indicates the concentration of PEDOT/PSS (in % volume). Table 1 shows the different formulations used in this study.

2.3. Water uptake measurements

The swelling capability of hydrogels was investigated by measuring their water uptake (WU) and using Eq. (1), where \(W_s\) and \(W_d\) are the weight of the swollen hydrogel at equilibrium and the weight of dry hydrogel, respectively:

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W_s = \frac{W_d}{W_d}
\]

2.4. Morphology of the hydrogels by SEM images

The morphology of the hydrogels was analyzed through 12-KeV scanning electron microscopy (SEM, Shimadzu, model SS 550) images. The hydrogels were immersed in distilled water at 25 °C up to swell at equilibrium (ca. 48 h). Next, the samples were removed and immediately frozen by immersion in liquid nitrogen. Thereafter, the frozen hydrogels were fractured and lyophilized in a freeze dryer (Christ Gefriertrocknungsanlagen) at −60 °C for 24 h. The dried-lyophilized hydrogels were gold-coated by sputtering before observation by SEM.

2.5. Stress–strain measurements

Mechanical tests were carried out by a texture analyzer (TA.TXT\(_2\) Stable Micro System, Haslemere, UK) equipped with a 10-N load cell and an automated frame with a 10-mm stroke. A strain rate of 0.01 mm s\(^{-1}\) was used. The stress–strain curves were recorded for all hydrogels.