

Temperature-sensitive PVA/PNIPAAm semi-IPN hydrogels with enhanced responsive properties

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Abstract

A series of temperature-sensitive hydrogels of semi-interpenetrating polymeric networks (semi-IPN) composed of poly(*N*-isopropylacrylamide) (PNIPAAm) and poly(vinyl alcohol) (PVA) were prepared by radical polymerization. The PNIPAAm networks were cross-linked by *N,N'*-methylenebisacrylamide in the presence of linear PVA. The reaction processes were investigated by rheometry using oscillatory deformation tests. It was found that gelations were very fast and the modulus reached equilibrium within about 12.5 min. The prepared semi-IPN hydrogels were characterized for their morphologies and thermal behaviors by scanning electron microscopy and differential scanning calorimetry, respectively. The interior network structures of the semi-IPN matrix became more porous with increasing PVA. In comparison to the conventional PNIPAAm gel, the newly reported semi-IPN hydrogels exhibited the same lower critical solution temperature. Their swelling properties, such as temperature dependence of equilibrium swelling ratio, shrinking kinetics and reswelling kinetics in water, were also studied. Experimental data indicated that the shrinking and reswelling rates of the semi-IPN hydrogels were much faster than those of the conventional PNIPAAm hydrogels. With this novel approach, water absorption and response properties could be adjusted by tuning the feed ratio of NIPAAm and PVA. These fast responsive hydrogels exhibited improved temperature sensitivity and swelling properties compared to the conventional PNIPAAm hydrogel, which would be critical and desirable for a gel to find potential applications in biomedical fields, such as drug delivery systems and sensors.

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1. Introduction

Recently, increasing attention has been paid to prepare novel “smart” materials, which can change their molecular configuration and result in volume phase transition in response to environmental stimuli, such as temperature [1], pH [2] and antigens [3]. A number of studies have been carried out to explore the applications of these kinds of materials in the biomedical and biotechnological fields, including controlled drug delivery, tissue engineering, gene transfection and sensors, due to their tunable and stimuli-responsive properties [4–10].

One of the most commonly investigated temperature-sensitive polymers is poly(*N*-isopropylacrylamide) (PNIPAAm), which exhibits a phase transition temperature, i.e., a lower critical solution temperature (LCST, ~32–34 °C) in water [11]. PNIPAAm chains are soluble in water at room temperature, while precipitating from water when increasing the water temperature to above the LCST. At this time, aqueous PNIPAAm solution becomes opaque due to the separation of polymer chains from the solution medium. Correspondingly, cross-linked PNIPAAm hydrogels exhibit a sharp temperature-dependent volume change, which results in the ability to absorb and retain large amounts of water at room temperature. PNIPAAm hydrogels, however, collapse and lose almost all contained water upon heating above the LCST. When transferring the swollen PNIPAAm gel from below to above LCST, a thick and dense layer forms on the surface of the gel due to the phase

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separation, which restricts the water molecules from diffusing out. As a result, the shrinking kinetics of conventional PNIPAAm hydrogels is relatively slow [12–14]. This shortcoming greatly limits their applications in some specific fields, such as on–off switches, sensors and artificial muscles, where a fast response rate is required.

To prepare temperature-sensitive gels with rapid response for a variety of industrial and biomedical applications, many strategies have been investigated, including tailoring the microstructure to prepare macroporous PNIPAAm by phase-separation techniques [15], introducing mobile grafted hydrophilic chains into the conventional PNIPAAm networks [16] and template polymerization [17]. Other methods, including the use of aqueous saccharides or salt solutions as reaction media [18–20] and the formation of IPN [21,22] structures, have also been explored to increase the response rate of the resulting PNIPAAm hydrogels.

An IPN is a material which comprises two or more networks which are fully or partially interlaced on a molecular scale but not covalently bonded to each other and cannot be separated unless chemical bonds are broken [23]. The most widely investigated IPN is composed of two independent polymers with different chemical compositions. If one polymer is linear and penetrates another cross-linked network without any chemical bonds between them, the IPN is called a semi-IPN. If both of the polymers are cross-linked, it is called a full-IPN. It is believed that the formation of an IPN structure can conserve the properties of both polymers, and the interlocked structure in the cross-linked networks enhances the stability of the materials, thereby ensuring the mechanical strength. Many researchers have prepared PNIPAAm-related IPN materials to improve the properties of PNIPAAm or to introduce other properties to PNIPAAm networks [24–26]. For example, poly(methacrylic acid)/PNIPAAm IPN hydrogels were synthesized by a sequential method and these hydrogels exhibited dual pH- and temperature sensitivity [24,25]. PNIPAAm was also introduced into a poly(acrylamide) (PAAm) network to achieve a combination of the thermosensitivity of PNIPAAm and the good mechanical properties of PAAm. The resultant hydrogels showed an improvement in their elastic modulus compared to PAAm and maintained the thermosensitivity of PNIPAAm [26]. The self-IPN hydrogels, in which both polymers are PNIPAAm, were also synthesized to improve the mechanical and responsive properties of PNIPAAm hydrogels [22]. Zhang et al. [21] have reported the synthesis and preliminary characterization of poly(vinyl alcohol) (PVA)/PNIPAAm semi-IPN hydrogels with an extremely fast response rate to temperature changes.

PVA is a water-soluble hydrophilic polymer, which has been extensively explored as a biomaterial, being used in drug delivery systems, sensors and surgical repairs because of its excellent mechanical properties, biocompatibility and nontoxicity [27]. Pure PVA hydrogels are not sensitive to environmental stimuli and conventional PNIPAAm hydro-

gels show a relatively slow response rate. Therefore, a need exists to combine the advantages of PVA and PNIPAAm to prepare a new kind of material. In this study, we chose a novel approach by incorporating PVA with different molecular weights and contents into a conventional PNIPAAm network to prepare PVA/PNIPAAm semi-IPN hydrogels. The aim was to investigate the influence of the molecular weight of PVA and the feed ratio on the properties of the resulting hydrogels. The gelling kinetics was monitored by rheology. The interior morphologies and LCST behavior were studied by scanning electron microscopy (SEM) and differential scanning calorimetry (DSC), respectively. The temperature dependence of the swelling ratio and the shrinking and reswelling kinetics of these PVA/PNIPAAm semi-IPN hydrogels were also characterized to determine their thermoresponse capability. Cytotoxicity was tested using fibroblast cells as the model and the results showed that these hydrogels are nontoxic.

2. Experimental

2.1. Materials

NIPAAm was purchased from Sigma–Aldrich Logistik GmbH (Schnelldorf, Germany) and purified by recrystallization in hexane. PVA (average mol. wt. 89,000–98,000, 99% hydrolyzed and average mol. wt. 146,000–186,000, 99% hydrolyzed), *N,N'*-methylenebisacrylamide (MBAAm), ammonium persulfate (APS) and *N,N,N',N'*-tetramethylethylenediamine (TEMED) were used as supplied by Sigma–Aldrich Logistik GmbH without purification.

2.2. Preparation of PNIPAAm/PVA semi-IPN hydrogels

The preparation is similar to that reported previously [21]. Briefly, the NIPAAm, MBAAm and PVA solutions were mixed, then APS and TEMED, as a pair of redox initiators, were added to the mixture to initiate the reaction. The polymerization and cross-linking were carried out at 16 °C for 17 h. Subsequently, the prepared gel samples were removed and immersed in distilled water for 4 days, during which time the water was changed repeatedly to wash away the unreacted monomers and other impurities. The conventional PNIPAAm hydrogel was synthesized by the same polymerization method but without adding the PVA. The sample codes and feed composition are listed in Table 1.

2.3. Rheological test

The gelation processes of the samples were monitored by a rheometer (Bohlin Rheometer CVO50, Bohlin Instruments, UK) in a parallel mode. The upper plate had a diameter of 40 mm and the distance between two plates was 500 μm prior to the addition of the reaction solutions. During the rheological measurements, a solvent trap was

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