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Swelling behaviors, tensile properties and thermodynamic studies of water sorption of 2-hydroxyethyl methacrylate/epoxy methacrylate copolymeric hydrogels

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Abstract

A series of copolymeric hydrogels based on 2-hydroxyethyl methacrylate (HEMA) and epoxy methacrylate (EMA) were synthesized by bulk polymerization. Swelling behaviors and tensile properties of hydrogels were studied. Dynamic swelling behaviors of copolymeric hydrogels indicate that the swelling process of these polymers follows Fickian behavior. The equilibrium water content (EWC) decreased and volume fraction of polymer in hydrogel (ϕ_2) increased with EMA content increasing due to its hydrophobicity. The increase of ionic strength of swelling medium or temperature results in a decrease in EWC and an increase in values of ϕ_2. Young's modulus and tensile strength of hydrogels, as well as effective crosslink density (v_e), increased as EMA content increased or ionic strength of swelling medium increased, attributing to increasing interaction between hydrophobic groups and polymer–polymer interaction with an increase in EMA content or in ionic strength. The polymer–solvent interaction parameter χ reflecting thermodynamic interaction was also studied. As EMA content, ionic strength of swelling medium or temperature increased, the values of χ increased. The values of χ and its two components χ_H and χ_S varied with increasing T. The negative values and trend of the enthalpy and entropy of dilution derived from values of χ_S and χ_H, could be explained on the basis of structuring of water through improved hydrogen bonding and hydrophobic interaction.

Keywords: 2-Hydroxyethyl methacrylate; Epoxy methacrylate; Hydrogel; Swelling behaviors; Tensile properties; Effective crosslinking density; Polymer–water interaction parameter

1. Introduction

Hydrogels are polymers in three-dimensional network arrangement, which could absorb and retain large amounts of water. In the polymeric network hydrophilic groups or domains are present which are hydrated in an aqueous environment thereby creating the hydrogel structure [1]. Polymer hydrogels have been proposed for many applications such as the controlled delivery of medicinal drugs, artificial muscles, sensors systems and contact lenses, and they have potential applications in structural materials. But their applications are limited

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due to their poor mechanical properties. To produce hydrogels with high mechanical strength, researchers have taken many approaches: (1) using special comonomers or altering their composition [2,3], changing the type and concentration of crosslinking agent [4,5], and optimizing polymerization conditions [6,7]; (2) introducing interpenetrating polymer networks (IPN) into hydrogels [8–12]; (3) synthesizing organic/inorganic nanocomposite hydrogels [13–15]; (4) adopting the method of material reinforcement [16,17].

Hydrogels based on 2-hydroxyethyl methacrylate (HEMA) have stronger mechanical properties than others, which could be strengthened by the methods such as bulk polymerization [7], copolymerization with hydrophobic monomers [18] or with rigid cyclic monomers [3,19], introducing IPN [20–22], and fiber reinforcement [17]. Hydrogels based on HEMA copolymerized with styrene (St), methyl methacrylate (MMA), *N*-vinyl-2-pyrrolidone (VP), 4-*t*-butyl-2-hydroxycyclohexyl methacrylate (TBCM), *cis*-1, 2-*bis*(2,3-epoxybutanoyloxy)-3,5-cyclohexadine (DHCD-EB), *n*-butyl methacrylate (BMA), cyclohexyl methacrylate (CHMA), triethylenglycol dimethacrylate (TEGDMA), and poly(ethylene glycol) methacrylate (PEGMA) have been prepared and studied [3,18,19,23–26]. But introducing a bisphenol A epoxy resin into hydrogels for strengthening has never been reported so far, although epoxy resin is widely applied in material science due to its high strength. As a particular macromonomer, epoxy methacrylate (EMA) (Fig. 1) obtained from bisphenol A epoxy resin and methacrylic acid, which has rigid structure of bisphenol A, could copolymerize with hydrophilic monomer 2-hydroxyethyl methacrylate (HEMA) to synthesize hydrogels with high strength. In addition, the macromonomer EMA also acts as a crosslinker because of its two methacrylate groups on two ends. We prepared a series of novel polymers based on EMA and HEMA by bulk free-radical polymerization, which were swollen in water to obtain hydrogels.

Previously, Huglin's group has studied hydrogel systems VP/HEMA, PVP, MMA/VP and *n*-butyl acrylate/*N*-vinyl-2-pyrrolidon (BA/VP) [2,23,27,28], and the latter two are hydrophobic/hydrophilic monomer pairs. In this paper, we would study the hydrogels with hydrophobic/hydrophilic monomer pair EMA/HEMA. The objectives of this work are: (1) to study the swelling and mechanical properties of hydrogels with various monomer composition; (2) to study the effect of monomer composition, ionic strength of swelling medium and temperature on network parameters such as effective crosslink density (v_e) and molar mass per crosslink (M_C); (3) to study thermodynamic interactions reflected by polymer–water interaction parameters (χ).

2. Experimental

2.1. Materials

2-Hydroxyethyl methacrylate (HEMA) was supplied by Tianjin Research Institute of Chemical Reagents, China; Epoxy methacrylate (EMA) was supplied by Wuxi Resin Plant, China; Benzoyl peroxide (BPO) and *N*,*N*-dimethylaniline (DMA) were used as oxidizer and reducer respectively, obtained from Beijing Chemical Reagents Co., China. All materials were used as received without further purification.

2.2. Preparation of polymers

Mixtures of HEMA and EMA were made up gravimetrically, 0.10 wt% BPO of monomers was added, bubbling with nitrogen for 20 min, and then the same amount of DMA as BPO was added. The solution was poured into a Teflon mould with 3 mm deep, sealed immediately. The whole process was carried out in protection of N_2 atmosphere. Then the mould was placed in an oven at 30 °C for 3 h. The xerogels were obtained after being removed from moulds. The weight ratio of EMA to HEMA were adjusted to 0/100, 5/95, 10/90, 15/85, 20/80, 25/75, 30/70. For these samples we named PHEMA, EMA5/HEMA95, EMA10/HEMA90, EMA15/HEMA85, EMA20/HEMA80, EMA25/HEMA75 and EMA30/HEMA70 respectively.

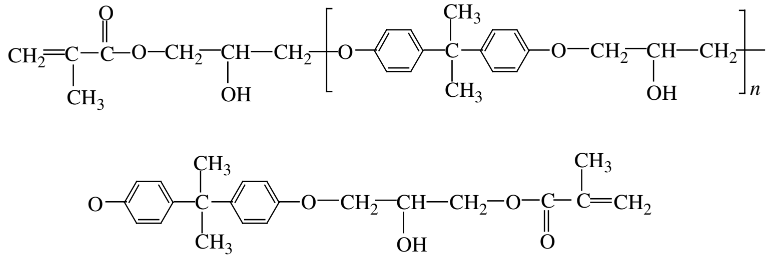

Fig. 1. Structure of epoxy methacrylate (EMA).