A novel designed high strength and thermoresponsive double network hydrogels cross-linked by starch-based microspheres

Chang Liu · Ying Tan · Kun Xu · Mei Hua · Xiao-Hui Huo · Yin-Shi Sun

Received: 10 April 2018 / Accepted: 25 September 2018 / Published online: 5 October 2018
© Iran Polymer and Petrochemical Institute 2018

Abstract
A new kind of nanocomposite double network (DN) hydrogels consisting of starch-based microspheres cross-linked oligo (ethylene glycol) methyl ether methacrylate (POEGMA) as soft network and diethylene glycol dimethacrylate (DEGMA) cross-linked poly(2-(2-methoxyethoxy) ethyl methacrylate (PMEO2MA) as brittle network (named POEGMA/PMEO2MA DN hydrogels) were synthesized by a two-step free radical polymerization. The chemical structure of DN hydrogels was characterized by 1H NMR, the temperature sensitive properties were measured by the lower critical solution temperature (LCST) tested by UV-Vis spectrophotometer as a function of temperature, the mechanical properties were measured by tensile test. The LCST showed only one transition at 20.2 °C measured by the transmittance variation as a function of the ambient temperature from 5 to 70 °C. The fracture toughness and the hysteresis behaviors were also tested and showed that they were affected by the content of starch-based microspheres cross-linker in the soft POEGMA network, the content of small-molecular cross-linkers and monomer concentration in the brittle PMEO2MA network. They are related to perfect network and physical adherence and entanglements between microspheres and the networks brought by AAS microspheres, the increment of “sacrifice bond” brought by DEGMA and polymer chains entanglement brought by MEO2MA. These studies will provide theoretical support for the future research of DN hydrogel and macromolecular microspheres cross-linked hydrogel.

Keywords Hydrogel · Thermosensitive · Double network · Microspheres cross-linked · Mechanical properties

Introduction

Hydrogels are three-dimensional networks formed by hydrophilic polymer chains, and consisted of a large amount of water [1, 2]. Thermoresponsive hydrogels are a kind of smart hydrogels, which can experience abrupt transition in volume, transmittance and other properties in response to mild temperature fluctuations. However, their poor mechanical properties limit their applications in artificial cartilage, tendons, muscles, and blood vessels. It is widely believed that constructing hydrogels with unique microstructures is a promising strategy to achieve hydrogels with excellent mechanical strength and may find successful applications as load-bearing biomaterials [3], such as double-network hydrogels (DN hydrogels) [4, 5], slide-ring gels [6], click gels [7], tetra-PEG gels [8], triblock copolymers hydrogels [9], nanocomposite hydrogels [10], ionically cross-linked hydrogels [11], ligand-cross-linked hydrogels [12, 13], hydrophobic modified hydrogels [14], macromolecular microsphere composite hydrogels (MMC hydrjogels) [15] and microgel-reinforced hydrogels [16, 17] etc.

Among them, adopting DN structure is an excellent method to enhance the toughness of hydrogels [18, 19]. Conventionally DN hydrogels have two networks, the first network is a tightly cross-linked hydrogel such as poly(2-acrylic acid amides-2-methyl propyl sulfonic acid) (PAMPS), and the second network is a loosely cross-linked hydrogel, such as polyacrylamide (PAM) [20]. Brown [21] and Tanaka [22] showed that the first brittle network will break up forming multiple micro cracks when the stress is above a defined value.