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The effect of cross-linker concentration on the physical properties of poly(dimethyl acrylamide-co-stearyl acrylate)-based shape memory hydrogels

M. Hasnat Kabir [a,*], Kumkum Ahmed [b], Hidemitsu Furukawa [b]

[a] Dept. of Information and Communication Engineering, University of Rajshahi, Rajshahi 6205, Bangladesh
[b] Soft and Wet Matter Engineering Laboratory, Department of Mechanical Systems Engineering, Graduate School of Science and Engineering, Yamagata University, 4-3-16 Jonan, Yonezawa City, Yamagata 992-8510, Japan

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ABSTRACT

Chemically cross-linked shape memory hydrogels were synthesized, and their physical properties were studied. The gels were made from a hydrophilic monomer, *i.e.*, N,N-dimethyl acrylamide (DMAA), and a hydrophobic monomer, *i.e.*, stearyl acrylate (SA). The properties were characterized by varying the concentration of the cross-linker methylene bisacrylamide (MBAA), whereas the concentrations of other chemical components were held constant. It was observed that the mechanical properties strongly depended on the cross-linker concentration. The cross-linked hydrogels showed improved toughness compared to the hydrogel counterparts without cross-linking. Thermal properties were investigated by differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA). DSC spectra of dried samples exhibited a complex crystalline nature, while swollen samples showed homogeneous crystallinity. The experimental results of DSC and TGA suggested that there was no significant influence of MBAA concentration on the crystallinity and thermal properties of swollen SMG hydrogels.

1. Introduction

A hydrogel is a three-dimensional polymer chain network that absorbs large amounts of water. The hydrophilicity of the chains and the degree of cross-linking control the amount of water in the hydrogel [1]. The physical and transport properties of the hydrogel also depend on the water content [2]. Yamada-Nosaka et al. have reported that three types of water are available in the hydrogel, *i.e.*, free water, intermediate water and bound water [3]. Among them, bound water is prominent in the hydrogel due to the capture of water by hydrogen bonds in the polymer chains. Therefore, highly hydrophilic gels lead to large amounts of bound water. Water-soluble hydrophobically modified acrylamide gels have various prospective applications such as biosensors [4–5], microencapsulation [6–7] and drug delivery [8]. The properties of a polymer gel depend on the chemical concentrations and the structures. The physical properties can be controlled by external stimuli, for instance, heat, optics, solvent, and pH.

Several thermoresponsive gels have been developed. Among them, poly-(N-isopropylacrylamide) (pNIPAAm)-based physical gels are the most studied because they have a sharp phase transition at 32 °C [9]. However, it was reported that this physical gel is composed of mechanically weak scaffolds [10]. Nevertheless, physical networks are often-encountered in the syneresis of the hydrogel [11]. Chemically cross-linkable pNIPAAm hydrogels have been developed and showed an enhancement in the Young's modulus due to the formation of covalent bonds and an increase of the transition temperature to 37 °C [12]. Although the pNIPAAm hydrogels improved mechanically due to the chemical cross-linking, the improvement is not sufficient for certain applications.

A series of works was reported by Osada and co-workers in which water-swollen hydrogels were prepared by copolymerizing acrylic acid (AA) with a hydrophobic acrylate containing long alkyl side groups. They used n-stearyl acrylate (SA) [13], 16-acryloylhexadecanoic acid (AHA) [14], and hexadecyl acrylate (HA) as side groups to form molecular and supermolecular ordered structures. These gels can show reversible order–disorder transitions at the melting temperature [15]. Below the transition temperature, they found that the poly(AA-co-SA) gel was crystalline and rigid with a Young's modulus of more than 10^7 Pa, whereas above that temperature, the gel became adequately soft and could be easily deformed. After cooling, the deformed gel became rigid and retained its deformed shape. The gel recovered its original shape when it was again heated above the transition temperature. This shape recovery phenomenon is called the shape memory effect. A shape memory gel (SMG) exhibits the shape memory effect by undergoing an ordered–disordered transition using external stimuli, such as temperature [16].

* Corresponding author.
E-mail address: hasnatkabir11@gmail.com (M.H. Kabir).

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As a smart material, shape memory hydrogels are well known. With an increasing demand of new material in different applications, hydrogels have become interesting materials due to their attractive properties. They have huge potentials in the fields of micro and nanotechnology. Due to its high transparency, the poly(dimethyl acrylamide-co-stearyl acrylate) (DMMA-co-SA)-based shape memory hydrogel can be a good candidate for optical applications. The functionality of this material as an optical lens was examined and reported in the literature [17]. With a suitable micro-electronic circuitry, this lens can become a smart lens. The transition temperature of this material is approximately 42.5 °C and is tunable to human body temperature. Therefore, biosensors and micro actuators provide alternatives to existing devices in the field of micro-nanotechnology, which can be used in biomedical applications.

Recently, chemical cross-linkers have been widely used to develop new hydrogels. The three-dimensional networks of chemically cross-linked hydrogels exhibit high mechanical strength because of covalent bond formation during the gelation process. The increase in the mechanical strength comes from the irreversible feature of a covalent bond [18–19]. It was also reported that the mechanical properties of the alginate hydrogels are generally controlled by the cross-linking density [20]. However, Matsuda et al. have reported that cross-linking suppresses the formation of an ordered structure in the gel but is able to affect the transition of the Young's modulus [21]. Although chemically cross-linked hydrogels have been extensively investigated, the effect of cross-links on physical properties is not yet fully understood. Therefore, it is important to investigate the effect of the cross-linker concentration on the physical properties of hydrogels.

We have recently prepared an SMG with N,N-dimethyl acrylamide (DMAA) instead of acrylic acid (AA), which was used by Osada. Our SMG (DMMA-co-SA), which is suitable for optical applications such as optical lenses, is transparent at both room and high temperatures [17]. In contrast, a previously prepared SMG was opaque [22]. In this case, we used methylene bisacrylamide (MBAA) as a cross-linker. The SMG (DMAA-co-SA) has been studied, and its physical properties, such as transparency, shape memory effect, diffusion mechanism and mechanical strength, have been characterized [16,17]; however, the effects of cross-linker concentration on the physical properties have not been specifically investigated. In this paper, we present experimental results on swelling and mechanical and thermal properties as a function of the cross-linker concentration. In this context, several samples were prepared with the same cross-linker, but the concentration was varied to elucidate the effect of cross-linker concentration on the physical properties.

2. Materials and synthesis

Shape memory gels (DMAA-co-SA) were prepared using two monomers *i.e.*, N,N-dimethyl acrylamide (DMAA) and stearyl acrylate (SA). The concentration of the monomers was fixed to make a one molar solution. The gel was prepared with a 3:1 ratio (DMAA: SA). Benzophenone was used as a photo initiator at a concentration of 0.1 mol%. The concentrations of the monomers and photo initiator were constant in all samples. However, methylene bisacrylamide (MBAA) was used as a cross-linker, and the concentration of MBAA was varied from 0.02 to 0.30 wt.%.

The SMG was synthesized using a simple bulk polymerization method. The monomers, cross-linker and photo initiator were mixed together according to their designated concentrations. To remove O_2 gas, the solutions were treated with N_2 gas for 30 min. Two pieces of glass molds covered by a PET film were sandwiched with a silicone rubber spacer and filled with the gel solution. After that, the molds were placed in a UV chamber (wavelength is 365 nm) for 18 h. Finally, the gels were swollen by dipping them into pure water for several days to achieve an equilibrium swelling state. All of the swollen gels were transparent, rubber-like and flexible.

3. Methods

3.1. Tensile test

Tensile measurements were carried out with the ORIENTEC testing machine (model STA-1150) using a 50 N load cell for tension. A dumbbell-shaped specimen (K6251-8) was used to cut the samples from a sheet of the SMG hydrogel. The size of the sample was 50 mm long, 4 mm wide and 2 mm thick, and the crosshead speed was 100 mm/min. The gauge length of the sample was 16 mm. All tensile measurements were performed in air at room temperature.

3.2. Thermal property analysis

Thermal properties including melting and crystalline behaviors of SMG for both cross-linked and uncross-linked gels were investigated using differential scanning calorimetry (DSC) (Seiko EXSTAR 6200) under a continuous N_2 gas flow with a flow rate of 100 mL/min. Both dry and water-swollen samples (under equilibrium) with and without cross-linking were investigated. A small piece of sample was placed on the DSC cell for analysis. The sample was first cooled to −50 °C with a ramping rate of −10 °C/min, followed by heating to 100 °C with a ramping rate of 10 °C/min. The melting and crystallization temperatures were determined by endothermal and exothermal peaks, respectively. Thermal stability of the samples was measured with a thermogravimetric analyzer (TGA) (Seiko EXSTAR 6300). A heating rate of 10 °C/min from 0 to 500 °C was applied. During the measurements, N_2 was used as the purge gas with a flow rate of 200 mL/min.

4. Results and discussion

To elucidate the impact of cross-linker concentration on the physical properties, SMG samples were swollen with pure water for several days to reach an equilibrium swelling state. The swelling ratio (SR) is defined here as the weight difference between the swollen and the dried sample divided by the weight of swollen sample. The swelling ratio of different samples as a function of cross-linker concentration is shown in Fig. 1. It is seen from this figure that the swelling ratio slightly decreases as the MBAA concentration increases between 0.0 and 0.05 wt.%, and afterward, the swelling ratio remains constant. This indicates that the MBAA concentration does not have any strong influence on the swelling ratio after a critical concentration. Notice here that 0.0 wt.% indicates that the sample was prepared without a chemical cross-linker, which actually became a physical gel. In gels, the cross-linker concentration is correlated to the density of cross-links. It has been reported that the concentration of the cross-linker affects the swelling and the

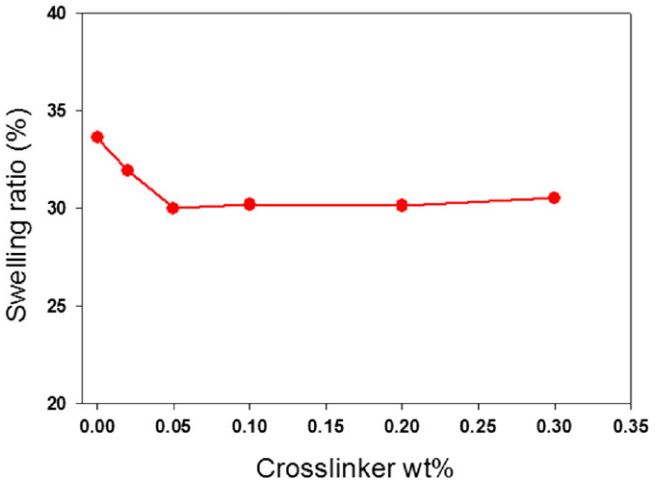

Fig. 1. The swelling ratio of SMG (DMAA-co-SA) as function of cross-linker concentration.