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Shape memory/change effect in a double network nanocomposite tough hydrogel

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ABSTRACT

In this paper, we present a systematic investigation on the shape memory/change effect in a double network nanocomposite tough hydrogel. Water-content dependency of the response of this hydrogel to heating and wetting by water is confirmed. Since this hydrogel is tough (even after being fully wetted in water) and has a relatively lower swelling ratio, apart from conventional shape memory/change effect as in ordinary hydrogels, additional features have been realized. These features include heating induced shape memory effect utilizing the absorbed water as the transition component, mechano-responsive shape change effect after water wetting and water-induced shape memory effect.

1. Introduction

Hydrogel is normally featured by its high volume expansion upon wetting in water (swelling). A number of applications, in particular in biomedical engineering in recent years, have been proposed based on this feature [1–7]. We have seen that great efforts have been dedicated to improve the performance of hydrogels in order to meet the needs of actual applications [2,7–10].

Shape memory effect (SME) refers to the ability of a material to recover its original shape only when the right stimulus, which includes heating/cooling, wetting in water or exposing to high humidity environment etc., is applied [11]. Recent study reveals that the heating/chemo-responsive SME should be the intrinsic feature of many polymeric materials, if not all [12].

Fundamentally, such a SME is different from the shape change effect (SCE), in which the shape of a material changes according to the level of the applied stimulus either proportionally (with/without hysteresis) in a linear/nonlinear manner or gradually in a viscous-elastic way [11,13].

As such, according to above definition, swelling phenomenon itself in hydrogels is essentially under the category of water-responsive SCE. Although the SME has been reported in some purposely synthesized hydrogels [14,15], our recent investigation reveals the water-content dependency of the heating/water (moisture)-responsive shape memory/change effect in a hydrogel and its composites [16]. That is to say, at an extremely low water-content (almost fully dry state), the hydrogel does not have either remarkable mechano-responsive SCE (as it is very stiff and a bit brittle) or the heating-responsive SME

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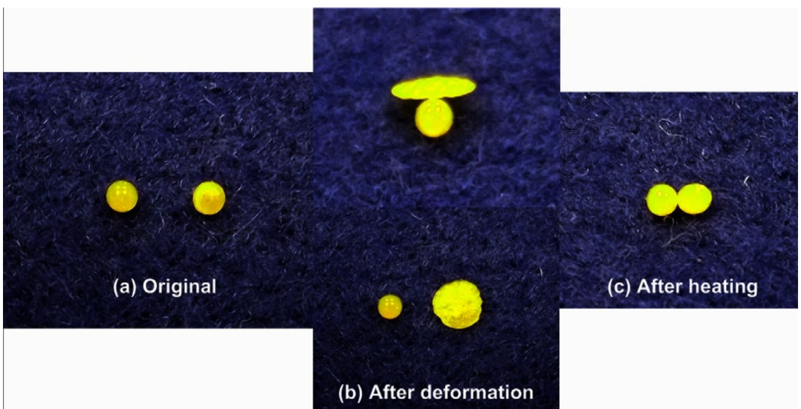
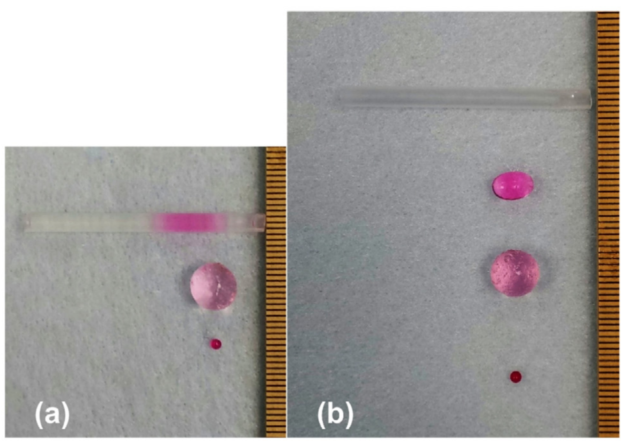
(since there is no transitions, either the glass transition or melting, as the required condition for the SME); at a relatively lower water-content, it has the heating-induced SME based on the glass transition; at a relatively higher water-content, it becomes rubber-like (mechano-responsive SCE); and at a very high water-content (so that apparent swelling is observed), it shows neither the heating-responsive SME nor the heating-induced SCE. By means of altering the actual water/moisture-content via wetting (in water or high humidity environment) or drying, a nice combination of both SME and SCE enables us to tailor the performance of a hydrogel for some special functions, which are not easily achievable based on only the SME or SCE. Similar phenomena have been reported in another hydrogel in [17], which demonstrates the generic nature of this finding.

As shown in Fig. 1(Ia), a hydrogel ball (same as that used in [16], in which the water content in weight fraction in fully wetted gel is more than 15,000%) is able to be easily flattened at above its glass transition temperature (T_g), if it is not very dry [Fig. 1(Ib), two views of a fattened piece from two different angles]. Only upon heating to above its T_g again, the flattened ball is able to almost fully recover its original shape [Fig. 1(Ic)]. On the other hand, if the hydrogel ball is wetted by water inside a straw [Fig. 1(IIa), top], so that its swelling induced expansion is limited in two directions, after it is wetted in room temperature (about 22 °C) water for a week and then removed out of the straw, the ball becomes elliptical shape and only the free expansion axis reaches the same dimension as that of the ball free from any constraint during wetting in water [Fig. 1(IIb)]. The elliptical shaped ball is able to gradually return its original ball shape and size upon drying without leaving any apparent permanent *damage* at all. However, if the straw is with some pre-cuttings, parts of the hydrogel ball may be cut out during swelling [18], since this hydrogel, if wetted in water, becomes brittle and fragile.

Fig. 2(a) compares the sizes of two square shaped hydrogel pieces, one is fully dried and the other is fully wetted. It should be point out that these two pieces have roughly the same size in the dry state. Although this hydrogel, which has been investigated in [17], is different from



(I)



(II)

Fig. 1. Heating-responsive SME (I) (another ball without flattening is included for comparison) and swelling with/without constraint (II) in a brittle hydrogel [for comparison, bottom small ball is dry one, and the big ball in the middle is fully wetted in room temperature (about 22 °C) water without any constraint].