

Preparation and Characterization of Temperature-responsive Gel Actuators by *in situ* Polymerization of N-isopropylacrylamide and Poly (vinyl alcohol)

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We describe the design and preparation of novel high-performance temperature-responsive gels for polymer actuators. A temperature responsive polymer was prepared by *in situ* polymerization of an N-isopropylacrylamide (NIPAAm) monomer in a dimethyl sulfoxide (DMSO) solution of poly (vinyl alcohol). The gels were prepared by casting a DMSO solution of the polymer obtained. The gels were annealed at 160°C and crosslinked in an ethylene glycol diglycidyl ether aqueous solution. A static stress-strain curve shows that the tensile strength and Young's modulus of the gel are over 5.7MPa and 0.8MPa, respectively. The gels swell at temperatures below the lower critical solution temperature (LCST) of PNIPAAm and shrink above the LCST. This phenomenon is observed reversibly. Under a load stress of 0.27MPa, the length change of the gel between at 15°C and at 50°C is more than 15%, and the maximum rate in swelling and in shrinking is 2.8% s⁻¹ and 8.5% s⁻¹, respectively. The gel's properties in the temperature- response and mechanical strength are enough to use for polymer actuators.

Key word: Gel, Temperature, N-isopropylacrylamide, Poly vinyl alcohol, Polymer actuator

1. INTRODUCTION

Recently, several researchers have studied on smart materials for actuators in order to prepare "artificial muscle" using shape-memory alloy [1-3] and ceramic [4,5]. Some of polymer gels swell and shrink in response to external stimuli, such as pH [6,7], temperature [8-14], electric fields [15-17] etc. These gels have potentials in applications for artificial muscles because they are soft, light and move with easy mechanism. Among all these external stimuli-responsive polymers, poly(N-isopropylacrylamide) (PNIPAAm) is the most widely studied polymer. PNIPAAm has a lower critical solution temperature (LCST) at around 32°C [18]. At temperatures below the LCST, PNIPAAm chains are well soluble in aqueous media so that a gel containing PNIPAAm chains is in a swollen state. When the temperature increases above the LCST, the polymer chains collapse and the volume of the gel dramatically decreases. The temperature-sensitive volume change of PNIPAAm gels can be applied in polymer actuators, artificial organs [19], on-off switches [20], immunoassays [21], drug delivery systems [22,23], separation processes [24,25]. For their practical usage, a fast response is needed. Since the swelling/deswelling rate of conventional PNIPAAm gels is ranging from hours to days, the gels are not satisfy the demands. Hence, several strategies have

been proposed to achieve fast responsive PNIPAAm gel [26-43]: (1) forming a heterogeneous network structure of the hydrogel using a phase separation method [26,27], γ -ray irradiation method [31], or use of a hydrophilic polymer as a pore-forming agent [29, 32, 42] and (2) preparation of a hydrogel having PNIPAAm chains grafted on the back-bone network, where the free ends of the graft chains acts to accelerate the dehydration rate [28-30]. For an ideal polymer gel for actuator, not only swelling/deswelling rate but also high mechanical strength is needed. However, it is still difficult to prepare a polymer gel having both fast response and high mechanical strength.

In a previous study, we prepared temperature-responsive polymer gels from NIPAAm, methacrylic acid and poly(vinyl alcohol) (PVA) [43]. The gels have higher swelling/deswelling rate and mechanical strength than conventional PNIPAAm gels.

In this paper, we prepare temperature-responsive polymer gels from PNIPAAm and PVA changing PVA content and the cross linking conditions and measure the water content, mechanical strength and swelling/deswelling behavior of the gels to obtain a polymer gel having high swelling/deswelling rate as well as high mechanical strength.

2. EXPERIMENTAL

2.1 Sample preparation

2.1.1 *In situ* polymerization

In order to obtain a temperature-responsive polymer, *in situ* polymerization of NIPAAm [N-isopropylacrylamide, Wako Pure Chemical Industries, Ltd.] was carried out in dimethyl sulfoxide [DMSO, Sigma Aldrich Japan] solution of PVA [poly(vinyl alcohol), Aldrich, Mw=85,000-146,000] using potassium peroxydisulfate as an initiator. The resulting polymer was precipitated in acetone solvent and was dried on a glass plate.

2.1.2 Preparation of temperature-responsive gels

Temperature-responsive gels were prepared by casting DMSO solution of the polymer obtained. The gels were annealed at 160°C for 20min in order to crosslink physically, and then crosslinked chemically in an ethylene glycol diglycidyl ether (EGDE) aqueous solution.

2.2. Measurement of the water content of the gels

The water content was measured as follows: the gels, weighted in the dry state, were immersed in an ion-exchanged water at several temperatures. The gels were removed from the water, tapped with filter paper to remove excess water on the gel surface, then the gels were weighted in the wet state. The water content, H , was calculated in term of

$$H = \frac{(W_w - W_d)/1.0}{(W_w - W_d)/1.0 + W_d/1.3} \quad (1)$$

where W_d and W_w are the dry weight and wet weight, respectively, and 1.0 and 1.3 are the densities of water and the polymer.

2.3. Measurement of the length change of the gels at different temperatures under a load condition

The length change of the gels under a load condition was measured using an apparatus shown in Figure 1. A 2.0cm × 1.5cm size sheet gel (thickness is 350 μm) was set in a water bath and one of the ends of the gel was fixed at the bath and the other end is connected to a load weight via pulleys using a string. First, the length of the gel at an equilibrium state in an ion-exchanged water at 15 °C was measured (L_0). Pouring hot water (50°C) and cold one (15°C) in the water bath alternately, the length change of the gels, L , was measured from the rotate angle of one of the pulleys. The length change is given from the following equation:

$$\text{Length - change} = \left(\frac{L}{L_0} \right) \times 100 \quad (2)$$

2.4 Measurement of the mechanical strength of the gels

Stress-strain curve of the gels was determined with a table model-testing machine (SHIMADZU, EZ-Test 500N). In the static stress-strain curve, specimens with a nominal 20-mm-gauge length and 0.2-mm thickness were deformed in tension at a constant strain rate of 10mm/min at 25°C, and stress-strain data were determined to failure. The tensile strength and Young's

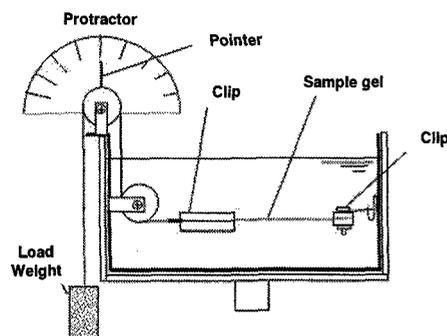


Fig. 1 An apparatus for measuring the length change of a sample gel between at 15°C and at 50°C under a load condition.

modulus of the gel was calculated from the stress-strain curve.

3. RESULTS AND DISCUSSION

3.1. Water content of the gel as a function of PVA content

Fig.2 shows the water content, H , of the gel as a function of PVA content, C_p , in the sample gels. The value of H at 15°C is higher than that at 50°C in all the PVA content. When the temperature is lower than the LCST, the polyNIPAAm is hydrophilic so that the water content is high. PolyNIPAAm become hydrophobic at temperatures above the LCST so that the gels have lower water content. The value of H both at 15°C and at 50°C increases with increasing C_p . The value at the high temperature increases more rapidly than that at the low temperature does. Hence, the difference of H between the two temperatures decreases with increasing C_p . Since the gels with less than $C_p=10\text{wt}\%$ do not have enough mechanical strength for polymer actuators, the values that C_p is around 15wt% will be the best condition for gels having both high swelling/deswelling ratio and high mechanical strength.

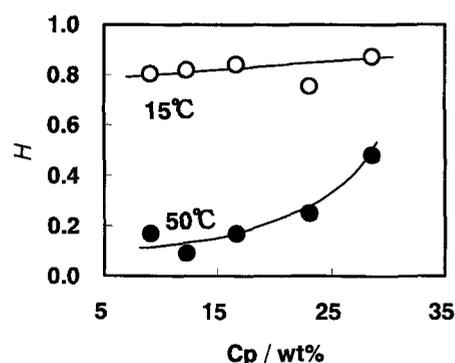


Fig.2 The water content of the gel, H , as a function of PVA content, C_p .

3.2. Tensile strength and Young's modulus of the gel as a function of the concentration of EGDE

Figure 3 shows the tensile strength and Young's

modulus of the gel as a function of the concentration of ethylene glycol diglycidyl ether, C_{EGDE} , in the crosslinking process. The Young's modulus increases with C_{EGDE} because the degree of crosslinking increases with C_{EGDE} . The value of the tensile strength also increases with C_{EGDE} and has a maximum when $C_{EGDE}=15\text{wt}\%$ and decreases because the gel with high degree of crosslinking is more brittle than that with low degree of crosslinking. The cross linked gel has 5.7MPa of tensile strength and 0.8MPa of Young's modulus when $C_{EGDE}=15\text{wt}\%$. These results indicate that the gels have enough mechanical strength for polymer actuators.

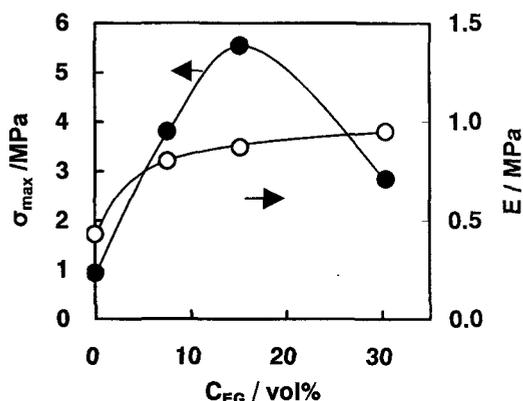


Fig.3 Tensile strength and Young's modulus of the gel as a function of the concentration of ethylene glycol diglycidyl ether, C_{EGDE} . The PVA content is 18wt% and the gels were crosslinked after annealing at 160°C.

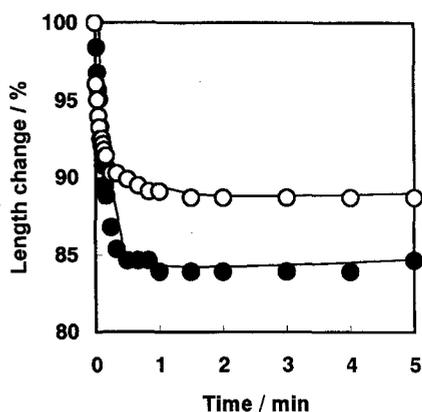


Fig.4 The deswelling curves of the gels in response to the temperature change from 15°C to 50°C. (○): annealed gel, (●): crosslinked gel with $C_{EGDE}=15.2\text{vol}\%$. Load stress=0.27MPa.

3.3. The effect of crosslinking conditions on the deswelling behavior of the gels in response to the temperature change

Figure 4 show the deswelling curves of the gels in response to the temperature change under a load condition of 0.27MPa. In the temperature-increase

process from 15°C to 50°C, both the gels deswell and the crosslinked gel changes its length more than 17% within 1 minute while the annealed gel does 12%. In the temperature-decrease process, whose results are not shown here, the crosslinked gel has higher values of both the rate and length change in swelling than the annealed one. This indicates that the crosslinking process with EGDE gives high swelling/deswelling properties to the gels.

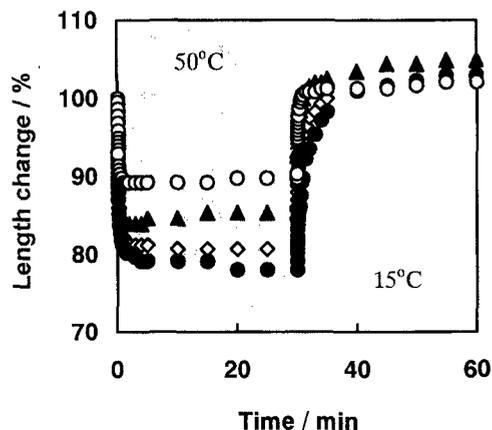


Fig.5 The swelling/deswelling behavior of the gels in response to the temperature change.

Load stress:

(●), 0.041MPa; (◇), 0.17MPa; (▲), 0.27MPa; (○), 0.28MPa. The gel was crosslinked with $C_{EGDE}=15.2\text{vol}\%$.

3.3. The swelling/deswelling behavior of the gels under various values of load stress

Figure 5 shows the swelling/deswelling curves of the gels in response to the temperature change under various values of load stress. The length change of the gels decreases with increasing the load stress and has a value of 10% under the load stress of 0.28MPa. The rate in both the swelling and deswelling process increase with increasing the load stress. The maximum rate in the swelling and the deswelling are $2.8\% \text{ s}^{-1}$ and $8.5\% \text{ s}^{-1}$, respectively, under the load stress of 0.27MPa.

3.4. The relationship between the maximum length change of the gels and load stress

The maximum length change of the gels between at 15°C and at 50°C in the swelling process is obtained from the swelling/deswelling curves and shown in Figure 6 as a function of load stress. The length change of all the gels between at 15°C and at 50°C is about 40% under no load stress and decreases with increasing load stress. The maximum length change of the crosslinked gel with $C_{EGDE}=15.2\text{vol}\%$ is higher than that of the annealed one in all the load stress. The value of the crosslinked gel with $C_{EGDE}=30.4\text{vol}\%$, however, lower than that of the annealed one. This is because

that the crosslinked gel with higher EGDE content is too rigid to change its length in response to temperature changes.

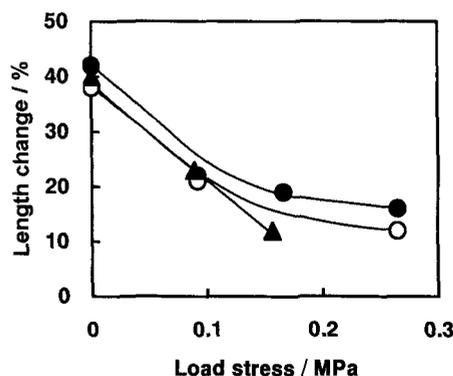


Fig.5 The relationship between the length change of the gels between at 15°C and at 50°C and load stress. (○), Annealed gel; (●), Crosslinked gel with $C_{EGDE}=15.2\text{vol}\%$; (▲), Crosslinked gel with $C_{EGDE}=30.4\text{vol}\%$.

4. CONCLUSION

We prepared a temperature-responsive gels from PNIPAAm and PVA, changing PVA content and EGDE concentration in the cross linking process. The gel containing 15wt% of PVA and crosslinked with 15.2vol% of EGDE solution has both high mechanical strength: 5.7MPa of tensile strength and high swelling/deswelling properties: the maximum rate of $2.8\% \text{ s}^{-1}$ and $8.5\% \text{ s}^{-1}$, respectively, in swelling and in deswelling under the load stress of 0.28MPa.

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