Improvement of Hot Water Resistance of Poly(vinyl alcohol) Hydrogel by Acetalization and Irradiation Techniques

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SYNOPSIS

In order to improve the heat stability of poly(vinyl alcohol) (PVA) hydrogel, acetalized PVA was irradiated with electron beam irradiation. The acetalization was strongly affected by PVA water content. There is an optimum water content of 20–30% for acetalization of PVA. The PVA gave maximum tensile strength at a dose of 100 kGy before or after acetalization. The PVA hydrogel maintained tensile strength of 10 MPa, even after 90 min boiling (98°C) in water or autoclave sterilization (121°C). It was confirmed that irradiation after, or before, acetalization is effective for enhancing heat resistance of a PVA hydrogel. The hydrogel is transparent, soft, has high tensile strength, and high hot water resistance.

INTRODUCTION

Hydrogel is a polymeric material (synthetic or natural) that swells when placed in contact with water but is not soluble and has the ability to retain water within its structure.

In recent years, much attention has been focused on the research and development of polymer hydrogels for biomaterials, such as contact lenses, wound dressing, enzyme immunoassay, catheters, and drug delivery systems (electric and temperature sensitive hydrogels, etc.).[1-3]

Poly(vinyl alcohol) (PVA) is a synthetic polymer that has excellent biocompatibility and is useful for medical purposes. The serious limitations of high water content hydrogels are poor mechanical properties such as low modulus of elasticity and tear strength that result in poor lens durability and handling characteristics. In addition, a hydrogel containing an ionic functionality poses a high affinity for protein.[4,5]

The hot water resistance of a hydrogel is particularly important when the hydrogel is sterilized by steam. Sakurada[6] mentioned that PVA fiber cross-linked (acetalized) with formaldehyde after heat treatment has good hot water resistance properties. It was also reported by Hirai[7] that PVA cross-linked with glutaraldehyde has shape memory properties.

In our previous work[8,9] a PVA hydrogel modified by radiation cross-linking after heat or by boric acid treatment, still results in poor heat resistance properties. To enhance the heat stability (hot water resistance) and physical properties of the PVA hydrogel, radiation cross-linking of acetalized PVA film was investigated in this study.

EXPERIMENTAL

Materials

PVA was supplied by Kuraray Co. Ltd. (Japan). It has a degree of polymerization of 1700 and a degree of saponification of 98–99%. Sulfuric acid (Wako Pure Chemical, Japan), formaldehyde solution (formalin content, 37%, Kanto Chemical Co. Ltd., Japan), and sodium sulfate anhydrous (Kanto) were used for acetalization. The water used in this experiment was distilled and all chemicals were analytical grade reagents.

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Preparation of PVA Hydrogel Film

An aqueous solution of PVA 20 wt % was prepared using an autoclave at 121°C for 50 min. The solution was then cast onto a glass plate at room temperature for a certain time to make a PVA sheet. PVA hydrogels were prepared by two methods. Method 1 is as follows: the sheet was acetalized by immersing in an acetalization bath containing aqueous formaldehyde, sulfuric acid, and sodium sulfate anhydrous (60 : 50 : 300 g) and 1 L water at 60°C for given times. Because the degree of acetalization is changed by temperature and concentration of sulfuric acid, formaldehyde, and sodium sulfate, temperature and concentration of such chemicals was fixed for acetalization. To remove the unreacted formaldehyde solution, the hydrogel film was rinsed with a water flow and then immersed again in water for 24 h, put into a polyethylene bag, and then nitrogen gas was introduced prior to irradiation. Method 2 is as follows: the PVA sheet was acetalized after irradiation. Irradiation and acetalization condition of the samples are the same as that of method 1. Irradiation was carried out using a beam current of 1 mA and an acceleration energy of 1 MeV generated by a Cockroft Walton Electron Beam Accelerator (2 MeV, 30 mA). After irradiation, physical properties such as tensile strength, gel fraction, and hot water resistance of samples was measured.

Tensile Strength and Elongation at Break

To provide an equilibrium condition, the hydrogel film was immersed in water at 25°C for 24 h. It was then cut into a dumbbell shape and physical properties such as tensile strength and elongation at break were measured using a Strograph-R1 tension meter (Toyo Seiki Co. Ltd., Japan) with a crosshead speed of 100 mm/min. The thickness of samples was 0.5 mm.

Degree of Swelling

The degree of swelling is defined as the ratio of the swollen gel mass to that of the dry gels. It was measured by allowing gel samples to equilibrate in distilled water in a thermostatically controlled water bath. Sample mass was determined by the blot-and-weigh technique. Dry gel mass was determined by drying the gel samples to constant mass in a vacuum oven at 65°C.

Hot Water Resistance

The hot water resistance of the PVA hydrogel was characterized by tensile strength and elongation at break properties after heating in boiling water (98–100°C) or in an autoclave for sterilization of medical devices at 121°C. After heating in a water bath or autoclave, the hydrogel films were immersed again in water at 25°C for 24 h, cut into dumbbell shape, and the tensile properties were measured as mentioned above.

Gel Fraction

To measure the gel fraction, a known weight of PVA (20 wt %) was prepared as previously mentioned. The sol fraction was removed by extraction in water using an autoclave at 121°C for 5 h. Then the gel was dried in a vacuum oven at 70°C. The gel fraction was defined as the ratio of dry gel mass to the initial mass of polymer:

$$\text{gel fraction (\%)} = (\text{weight of dry gel/weight of initial polymer}) \times 100.$$

RESULTS AND DISCUSSION

Appearance of PVA Hydrogel

The appearance of the hydrogel, particularly shape deformation, was identified visually. It was found that the hydrogel with a water content of more than 20% before acetalization became opaque and shrank after acetalization. On the other hand, if the water content was less than 20%, the hydrogel was transparent and the original film was unchanged even after boiling in water for 90 min.

Effect of Water Content on Acetalization

Evaluation of the mechanical properties of a PVA hydrogel is essential for application in medical devices especially in the swollen condition.

The usefulness of formaldehyde to improve the hot water resistance and the dyeability of PVA fibers has been investigated by many authors.[6,7,10,11] The relationship between hydrogel water content and tensile strength in acetalization is shown in Figure 1. It can be seen that the maximum tensile strength was found at water contents of 20–30%. Sakurada[6] mentioned that the acetalization reaction takes place in the amorphous portion of the polymer. The x-ray crystal diffraction pattern of PVA filaments before or after acetalization is essentially the same, which indicates that the crystalline part does not participate in the reaction. Thus, it is speculated that the

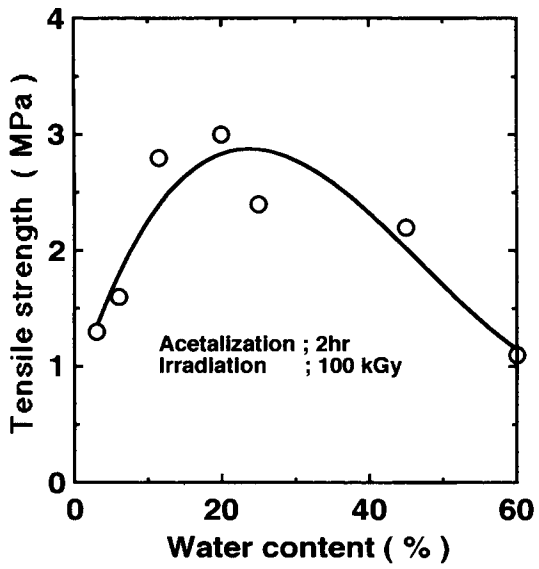

Figure 1 Effect of water content during acetalization for preparation of PVA hydrogel, on tensile strength.

amorphous portion is optimum in the range of 20–30% of PVA water content for tensile strength.

Irradiation Effect Before or after Acetalization on PVA Hydrogel

The effects of irradiation before or after acetalization on tensile strength of hydrogel are shown in Figure 2(a,b). The tensile strength increases up to 100 kGy and then decreases as the dose increases. At doses of 200 and 300 kGy, the tensile strength is lower and the hydrogel becomes brittle and stiff because of higher cross-link density. Natural rubber latex gives products such as surgical rubber gloves and balloons by the dipping method after sulfur vulcanization (cross-linking of rubbery or elastomeric material is termed vulcanization). We found that vulcanization of natural rubber latex by irradiation instead of sulfur is useful for enhancing physical properties of rubber film.[12,13] In this case, a maximum in tensile strength of the rubber film was observed vs. dose. Hence, it is assumed that a suitable cross-link density to give higher physical properties exists in irradiation of other polymeric materials containing water.

Hot Water Resistance by Boiling in Water

The hot water resistance is the ability of hydrogels to retain their shape and tensile strength properties against high temperature in a water medium, such as boiling water bath (98–100°C) or autoclave (121°C).

Figure 3 shows the tensile strength after boiling a PVA hydrogel in water prepared by irradiation after acetalization. Without acetalization and irradiation, the hydrogel melted under boiling treatment; the hydrogel irradiated at 100 kGy gave the tensile strength of 0.6 MPa, but this hydrogel film is soft and easy to break. According to these results, in both cases with and without irradiation, the tensile strength increases with increasing acetalization time and then levels off at around 35 h. It can be seen that hot water resistance is much improved not only by acetalization but also by irradiation. Hydrogel irradiated at 100 kGy after acetalization for 35 h has 20 MPa strength. Although the tensile strength of the hydrogel was reduced considerably in boiling water for 15 min, a tensile strength of 10 MPa remained. In contrast the tensile strength of the hydrogel without irradiation after acetalization was reduced to 4 MPa. From these findings, it was ascertained that irradiation after acetalization is useful in the enhancement of hot water resistance of the hydrogel. Figure 4 shows elongation at break after boiling in water for 15 min of irradiated hydrogel after acetalization. The elongation of the hydrogel before boiling in water decreased with increasing acetalization times and then became constant. This is due to the increase of cross-link density. On the other hand, the elongation of the hydrogel after boiling in water increased up to around 10 h acetalization and then leveled off with increasing acetalization time. The elongation of the hydrogel after acetalization for 10 h was around 300% both before or after boiling in water.

Hot Water Resistance by Autoclave (121°C)

Medical materials are often sterilized by autoclave (121°C). Thus, examination of heat stability of the hydrogel by autoclave is necessary. Figure 5 shows the tensile strength and elongation at break of the hydrogel irradiated at 100 kGy after 24 h acetalization in different autoclaving or boiling times, respectively. The tensile strength of the hydrogel reduces significantly by boiling or autoclaving treatments at an earlier stage, from around 20 MPa to around 10 MPa. The gels prepared by acetalization and/or irradiation have either hydrogen bonding and chemical cross-linking such as covalent bonding. By boiling in water, the hydrogen bond is destroyed, although chemical cross-linking remains in the gel. Thus, it is deduced that destroying hydrogen bonds causes a reduction in tensile strength properties.

Extending time of boiling in water to 90 min does not significantly affect the tensile and elongation properties. In the case of autoclaving, for which the

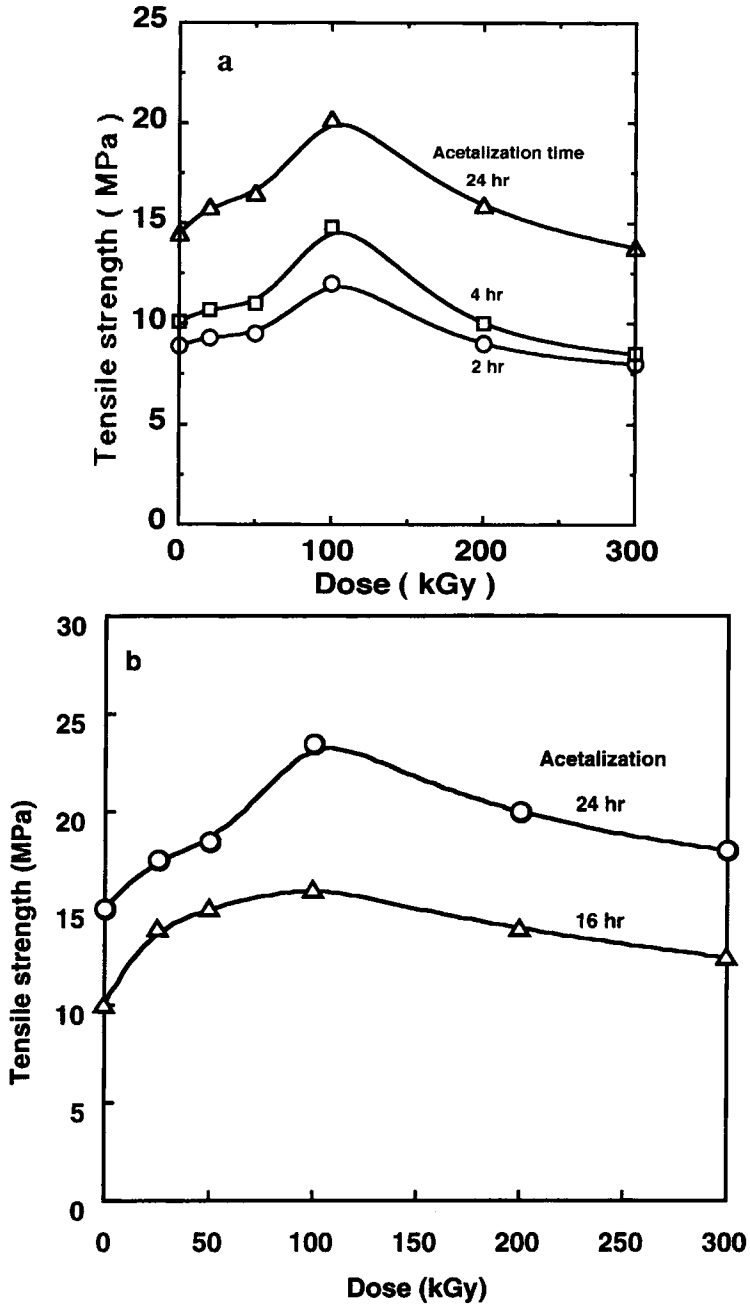

Figure 2 Tensile strength of PVA hydrogel obtained by irradiation (a) after or (b) before acetalization.

heating temperature is 121°C, the tensile strength decreases slightly as the time is extended. The tensile strength is 9.2 MPa even after 90 min autoclaving. Accordingly, it is concluded that a hydrogel prepared by the combination of acetalization and irradiation is sufficiently durable for autoclave and boiling sterilization. According to Figure 5, elongation at break of the hydrogel increases slightly by autoclaving; for boiling the elongation does not change vs. boiling time. The elongation of an irradiated hydrogel after acetalization is slightly greater in autoclaving compared to boiling in water, possibly because of the higher temperature.

Contribution of Irradiation on Gel Formation

In order to elucidate heat stability of a hydrogel prepared by the combination of acetalization and ir-

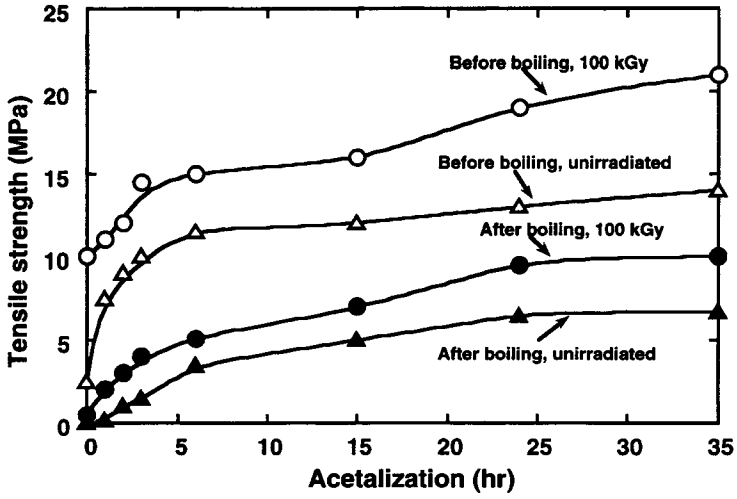

Figure 3 Evaluation of heat stability by boiling in water of PVA hydrogel. Boiling time, 15 min.

radiation, gel fraction was measured. The results are shown in Figure 6. The hydrogel acetalized even without irradiation formed a network structure, and gel of 100% was formed at an acetalization time of 24 h. On the other hand, higher gel formation for shorter acetalization time was observed by irradiation. From this finding, formation of PVA gel after acetalization was accelerated by irradiation. Although PVA gel of 100% is formed by cross-linking after 24 h acetalization, even without irradiation, the hot water resistance was lower than the hydrogel irradiated after acetalization (Fig. 3). This means that hot water resistance of the PVA hydrogel was improved by the combination of acetalization and irradiation. Network structure (cross-linking) of PVA is formed by irradiation without acetalization in the swollen state; however strength of the PVA sheet is low for extensive swelling in boiling water. Acetalization is preferred for improvement of hot water resistance of the hydrogel. By irradiation, hot water resistance of acetalized PVA was further improved. The electron beam irradiation technique is often used to improve heat resistance of polyolefin covered electronics wire. In this case, cross-linking takes place by recombination of radicals formed in the polymer chain by irradiation. Thus, —C—C—

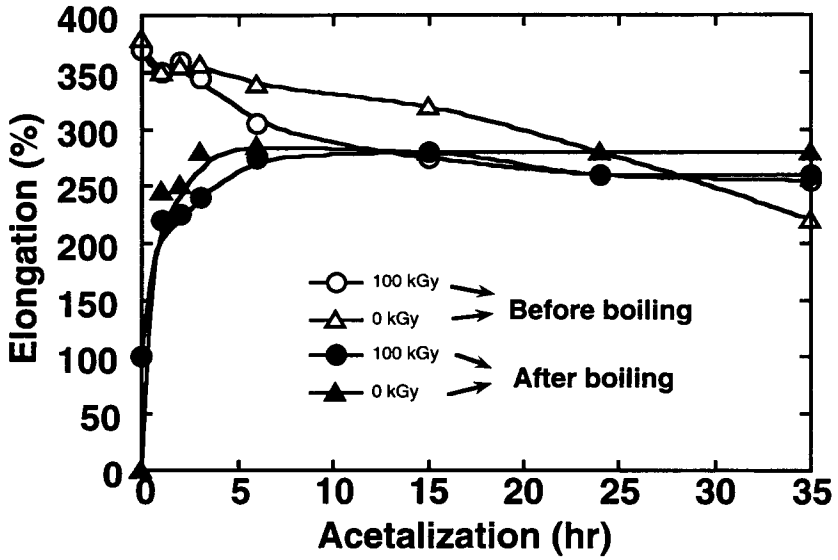

Figure 4 Elongation at break of PVA hydrogel before or after boiling in water for 15 min.

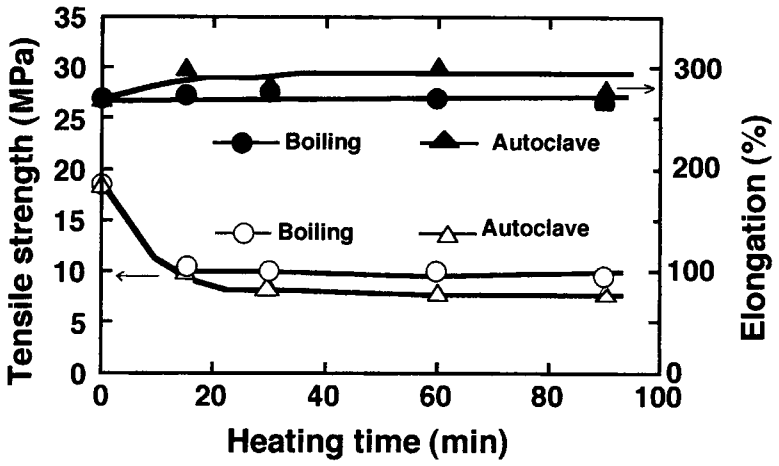

Figure 5 Tensile strength and elongation at break of PVA hydrogel after boiling or autoclaving for up to 90 min.

bond cross-linking of the PVA hydrogel is achieved by such a mechanism. On the other hand, in acetalization, intramolecular acetalization of the 1,3-glycol group and 1,2-glycol group and intermolecular acetalization take place between PVA and aldehyde (formaldehyde).[14] It is suggested that intermolecular acetalization contributes to improve physical properties of PVA. Accordingly, it is concluded that a PVA hydrogel that has elasticity and heat resistance is obtained by combination of —C—C— cross-linking by irradiation and —C—O—C— cross-linking by acetalization.

Swelling Properties of PVA Hydrogel

The swelling property of the PVA hydrogel is shown in Figure 7. The hydrogel to determine swelling property was prepared by irradiation of acetalized PVA film. The degree of swelling of hydrogel irradiated at 100 kGy after acetalization for 24 h at 60°C was 1.2. It became around 1.7 after boiling in water or autoclaving for 15 min. The degree of swelling was constant even if boiling and or autoclaving times were extended up to 90 min.

CONCLUSIONS

Studies on heat stability in boiling water or autoclave sterilization on PVA hydrogels for medical purposes have been carried out by irradiation techniques. It

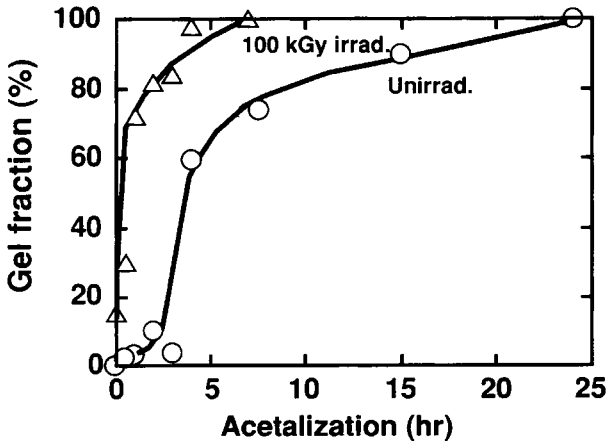

Figure 6 Gel fraction of PVA hydrogel irradiated at 100 kGy after acetalization.

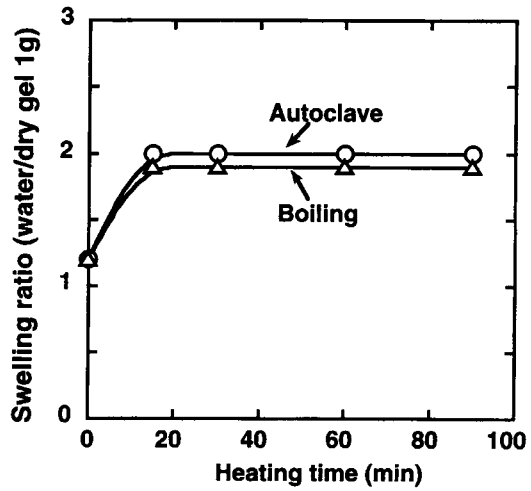

Figure 7 Degree of swelling after boiling or autoclaving of PVA hydrogel irradiated after acetalization. Dose, 100 kGy; acetalization, 24 h.

was found that irradiation before or after acetalization was effective in enhancing heat stability of PVA hydrogels. The dose to give maximum tensile strength of the hydrogel after acetalization was 100 kGy.

After boiling or autoclave sterilization, PVA hydrogels obtained by 100 kGy irradiation after acetalization of 24 h have 10 MPa strength and around 270–320% elongation.

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