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Adhesion of poly(vinyl alcohol) hydrogels by electrophoretic manipulation of phenylboronic acid copolymers

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With an aim to develop 3D soft materials with biocompatibility and non-toxicity properties, in this study, we attempted the rapid adhesion of poly(vinyl alcohol) (PVA) hydrogels to each other by using an electric field and water-soluble intermediate phenylboronic acid copolymers. The PVA hydrogels adhered to each other following electrophoretic manipulation of poly(3-methacrylamidophenylboronic acid-*co*-*N*,*N*-dimethylacrylamide) copolymers at the interface of the PVA hydro gels. The adhered PVA interface was stable under the physiological conditions, but detachment was observed in the presence of an excess amount of sugar and acid. Detached gels re-adhered under the same conditions, indicating that the adhesion of the hydrogels exhibits repeatability. Electrophoretic adhesion of PVA and related hydrogels may be useful in the field of tissue engineering for the development of on-demand 3D scaffolds.

Introduction

Hydrogels have attracted much attention in the field of tissue engineering for their ability to form three-dimensional (3D) scaffolds due to their high water content and flexibility.[1] Poly(vinyl alcohol) (PVA) is a well-known biocompatible and non-toxic material, often studied in the biomaterial field.[2, 3] Chemically cross-linked gels with glutaraldehyde and/or poly(ethylene glycol)diglycidyl ether and physically cross-linked PVA hydrogels are used as cell culture matrices.[4-6] Adhesion of PVA hydrogels may be a convenient method for the construction of 3D scaffolds for cell culture. Although adhesion by interactions between two hydrogels, such as metal-ligand[7], electrostatic[8-11], host-guest[12], and organic-inorganic[13-16] interactions, have been reported, this often proves difficult because PVA hydrogel only have hydrocarbons in the polymer backbone and hydroxy groups in the side chain. Studies on adhesion of PVA hydrogels have also been reported using hydrogen bonding; for example, self-healing properties have been found to physically cross-linked PVA hydrogels.[17] However, the complete adhesion through the self-healing process takes few hours to an entire day, and aged surfaces do not adhere to each other. Moreover, hydrogel scaffold with a specific spatial configuration are difficult to prepare with the spontaneous adhesive method. For the fabrication of on-demand scaffold using PVA hydrogels, a stimulus-responsive adhesive method that can work well under physiological conditions is required.

To study interactions of the hydroxy groups of PVA, we focused our attention on phenylboronic acid (PBA). It is well known that PBA groups show reversible bonding with diol units around the pK_a of PBA, and PBA units are used as sensing moiety for targeting diols such as glucose[18-22], and assembling of nanoparticles[23]. Moreover, PBA-functionalized polymers such as polymeric micelles[24] and hydrogels[25] have been developed as carriers for siRNA and cells, respectively, in the field of biomaterials. Other researchers reported that PBA copolymer hydrogels adhere to catechol-containing hydrogels under high pH conditions.[26] This process is reversible as a result of the exchange reaction of sugar and diol with phenylboronate. However, to our best knowledge, adhesion of chemically cross-linked PVA hydrogels to each other has not been achieved, although hydrogels have been formed by mixing aqueous PBA copolymers and PVA linear chains.[25] If the adhesion of PVA hydrogels can be controlled, biocompatible and non-toxic 3D constructs[27-29] could be created.

We recently reported the rapid adhesion of hydrogels by using an electrophoretic technique.[30-34] Alternating-current (AC) electrophoretic adhesion of similarly charged hydrogels was achieved with oppositely charged water-soluble polymers as a binder.[34] Two anionic hydrogels adhered to each other when the AC electric field was applied with a square wave when a cationic polymer solution was sandwiched between the two anionic hydrogels, although adhesion of the two anionic hydrogels utilizing cationic polymers as binders was not observed when a direct-current (DC) electric field was applied. Therefore, oscillation of the cationic polymer at the interface was necessary for the formation of the polyion complex and hydrogel adhesion during AC electrophoresis. This electrophoretic adhesion of hydrogels may be used not only for the combination of oppositely charged polymers but also for diol and phenylboronate complexes because

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phenylboronate is weakly charged in an aqueous solution around their pK_a. Therefore, the simple and rapid adhesion of PVA hydrogel constructs may be achieved by using PBA copolymers.

In this study, for the development of biocompatible and non-toxic 3D soft materials, we demonstrated the rapid adhesion of PVA hydrogels by electrophoretic manipulation of intermediate water-soluble PBA copolymers at gel interfaces. The adhesive strength of the reversible covalent bond of the adhered PVA hydrogels using PBA copolymer was investigated. We also studied the stability of the adhered gels under physiological condition in the presence of sugar.

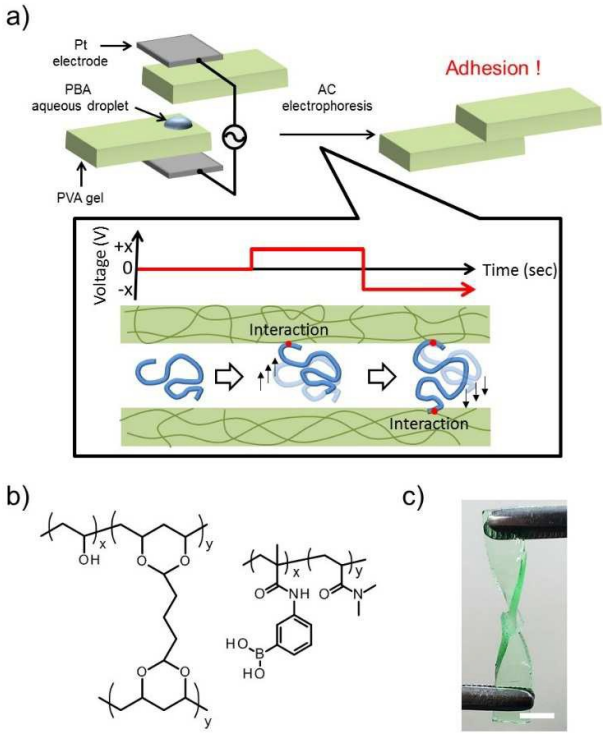

Fig. 1 (a) Schematic illustration of AC electrophoretic adhesion of poly(vinyl alcohol) (PVA) hydrogels by manipulation of intermediate poly(3-methacrylamidophenylboronic acid-*co*-*N*,*N*-dimethylacrylamide) (PBA) copolymers. PBA copolymers oscillated during AC-electrophoresis and interacted with PVA gels. (b) Chemical structure and (c) image of adhered PVA/PVA hydrogels utilizing PBA copolymers. PVA hydrogels were stained with a green dye. The scale bar represents 5 mm.

Experimental

Materials

Poly(vinyl alcohol), 3-methacrylamidophenylboronic acid, *N*,*N*-methylenebis(acrylamide), methanol, glutaraldehyde, glucose, fructose, and sorbitol were purchased from Wako Pure Chemical Industries (Osaka, Japan) and used as purchased without further purification. *N*,*N*-Dimethylacrylamide and 2,2'-azobis(isobutyronitrile) (AIBN) were purchased from Wako Pure Chemical Industries and used after distillation and recrystallization, respectively.

Preparation of poly(3-methacrylamidophenylboronic acid-co-*N*,*N*-dimethylacrylamide) (PBA) copolymer

The copolymerization of 3-methacrylamidophenylboronic acid and *N*,*N*-dimethylacrylamide was carried out in methanol using 1mol% AIBN as an initiator under nitrogen atmosphere at 60°C for 4 h. The product was obtained by lyophilization after the polymer was dialyzed using a Spectra/Por regenerated cellulose membrane (molecular weight cut-off of 3,500) in $NaHCO_3$ aqueous solution and water consecutively. The chemical structure of the PBA copolymer was confirmed by proton nuclear magnetic resonance (^{1}H-NMR) spectroscopy. Products are coded as PBA_x, where *x* is the molar ratio of phenylboronic acid in the copolymer.

Preparation of poly(vinyl alcohol) (PVA) hydrogels

Chemical cross-linked PVA hydrogel was prepared as nonionic gels. Glutaraldehyde (1 mol% to the vinyl alcohol units) and hydrochloric acid were added to 10 mL of 10 or 20 wt% PVA aqueous solution. The aqueous solution was injected into glass plates with 1 mm spacing and the cross-linking reaction was carried out at ambient temperature. The prepared hydrogel was washed with water for the removal of unreacted glutaraldehyde and hydrochloric acid. Swelling ratios (SRs) of the hydrogels were determined as the ratio of the weight of the swelled gels (W_s) to the weight of the dry gels (W_d): $SR = (W_s - W_d)/W_d$. Tensile strength (TSs) was measured using a tensile tester (Shimadzu EZ-S10) in an ambient atmosphere. They were loaded to failure at 1 mm s^{-1} in tensile mode, and the failure strain was measured.

Adhesion of hydrogels

PBA copolymer was dissolved and PVA hydrogel was swelled in phosphate buffer (PB: pH=7.2, *I*=0.015). To adhere the PVA hydrogels to each other, an aqueous PBA copolymer solution (1 g L^{-1}, 5 μL) was dropped onto the hydrogel interface. The hydrogels were held in contact with each other in between two Pt electrodes, and alternative electric field with a square wave was applied. The adhesive strength was measured using a tensile tester as the lap shear adhesion force in an ambient atmosphere. The adhered gels were held at both ends of the supporting plates with two mechanical chucks. They were loaded to failure at 1 mm s^{-1} in tensile mode, and the failure strain was measured.

Stability of adhered gels immersed in a sugar solution

Adhesion stability was evaluated in the presence of sugar such as glucose, fructose, and sorbitol. Adhered PVA hydrogels were immersed into 0.00 (without sugar), 0.01, 0.10 and 1.00 mol L^{-1} sugar aqueous solution (phosphate buffered saline: PBS) for 24 h, and a tensile testing was carried out.

Results and discussion

The adhesion of PVA hydrogels was carried out by using an intermediate PBA copolymer as binder and AC electric field (**Fig. 1a**). Poly(3-methacrylamidophenylboronic acid-*co*-*N*,*N*-dimethylacrylamide) [poly(MAPBA-*co*-DMAAm)] was by prepared radical copolymerization of DMAAm and PBA and *N*,*N*-dimethylacrylamide were used as hydrophilic and neutral units. PVA cross-linked with glutaraldehyde was prepared as nonionic hydrogel **(Fig. 1b)**. The values for SR and TS were as follows: SR = 14.2 ± 0.3 and TS = 17.5 ± 4.4 kPa for the 10 wt% PVA hydrogels, and SR = 8.9 ± 1.0 and TS = 38.1 ± 7.8 kPa for the 20 wt% PVA hydrogels. A lower SR and higher TS were obtained by increasing the PVA concentration from 10 to 20 wt%. The chemical composition of PBA copolymers is summarized in **Table 1**. As shown in **Table 1**, the degree of PBA into copolymer was modulated in feed, and the copolymer with 16.8% of PBA was insoluble in phosphate buffer (pH=7.2, *I*=0.015) due to the hydrophobicity of the PBA units, because the pK_a value of methacrylamidophenylboronic acid is 8.6.[19] Therefore, 3.5%, 6.0%, or 10.2% PBA in copolymer was used for the adhesive experiments because they were soluble in phosphate buffer. For adhesion of PVA hydrogels, $PBA_{3.5}$, $PBA_{6.0}$, or $PBA_{10.2}$ copolymers was dropped on one of the PVA hydrogel surface, followed by the placement of the other PVA hydrogel on top. The two PVA hydrogels adhered to each other within 10 sec when AC voltage was applied with square wave (**Fig. 1c**), while two PVA hydrogels did not adhere by pressure bonding or DC voltage impression.

Table 1. Preparation of water-soluble PBA copolymers [a]

Run	Feed ratio MAPBA:DMAAm	PBA in copolymer[b] (mol%)	yield (%)	Solubility of copolymer in phosphate buffer[c]
1	5:95	3.5	96	o
2	8:92	6.6	89	o
3	10:90	10.2	95	o
4	15:85	16.8	78	x

(a) Polymerization was carried out in methanol using 1mol% AIBN as initiator under a nitrogen atmosphere at 60°C for 4h. (b) As determined by ^{1}H-NMR in D_2O. (c) o: soluble, x: insoluble

On the other hand, PVA hydrogels and PBA containing hydrogels adhered each other by DC voltage impression (**Fig. 2**). To make poly(MAPBA-*co*-DMAAm) (PBA) hydrogel **(Fig. 2a)** and PVA hydrogel adhere, they were held in contact in between two Pt electrodes, and an electric field was impressed. The PBA and PVA hydrogels adhered when an electric field was applied, with the cathode on the PBA hydrogel and the anode on the PVA hydrogel **(Fig. 2b)**. No adhesion of the two hydrogels was observed with the opposite electric field impression and/or pressure bonding. These results indicate that the amount of phenylboronate is insufficient for the adhesion of these hydrogels. Previously, we reported the electrophoretic adhesion of oppositely charged hydrogels.[30, 31, 33] The cationic and anionic hydrogels in contact adhered when a direct-current (DC) electric field was applied, with cationic and anionic hydrogel at the anode and the cathode, respectively. Because the positively and negatively charged segments inside the hydrogels moved to the cathode and anode, respectively, a polyion complex (PIC) was formed at the hydrogel-interface for adhesion of the two hydrogels through electrophoresis. Therefore, in this study, anionic charged phenylboronate may move to the anode during electrophoresis and bound to PVA diols for adhesion. Detachment of adhered gels was not observed during an opposite electric field impression, indicating that charged phenylboronate formed covalent bonds with PVA diols at the interface of the two hydrogels by electrophoresis. Three-layered PVA/PBA/PVA hydrogels were also prepared when an AC electric field was applied (**Fig. 2c**). These results indicate that both PBA linear polymer and hydrogels act as binders for the adhesion of PVA hydrogels.

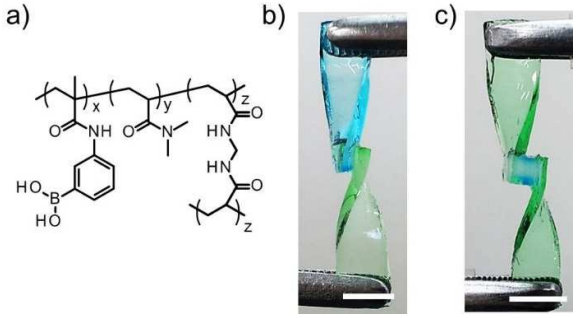

Fig. 2 (a) Chemical structure of poly(3-methacrylamidophenylboronic acid-*co*-*N*,*N*-dimethylacrylamide) (PBA) hydrogels and adhered (b) PBA/PVA and (c) PVA/PBA/PVA hydrogels. The PBA and PVA hydrogels were stained by blue and green dye, respectively. All scale bars represent 5 mm.

The adhesive strength of PVA/PVA hydrogels was measured by a loading to failure tensile test, as shown in **Fig. 3**. PVA hydrogels (20 wt%) were used because of their higher tensile strength. The adhesive strength of adhered gels increased while increasing PBA contents into the copolymer as binders (**Fig. 3a**). When a voltage was impressed to a PBA copolymer sandwiched in between PVA hydrogels, the negatively charged PBA copolymer moved to the anode by electrophoresis, and the PBA units reacted with diols of the PVA hydrogel interface. Continuously, partially bonded PBA copolymers on the PVA surface move to opposite side of PVA hydrogels by inverse voltage impression, and then two PVA hydrogel adhered to each other utilizing PBA copolymer (**Fig. 1a**). Therefore, the adhesive strength increased with increasing impressed voltage when the $PBA_{6.0}$ copolymer was used as binder (**Fig. 3b**), because the polymer mobility was proportionate to the applied voltage. These results are in good agreement with a previous study using electrostatic interaction and indicate that both the mobility of the PBA copolymers and the interaction of PBA with PVA play a key role in the adhesion of PVA hydrogels, with oscillating PBA copolymers stepwise-interacting with diols at the interface of the PVA hydrogels during AC electrophoresis (**Fig. 4**). Adhesive strength of PVA hydrogels was controlled by not only the amount of phenylboronate but also the electrophoresis condition.

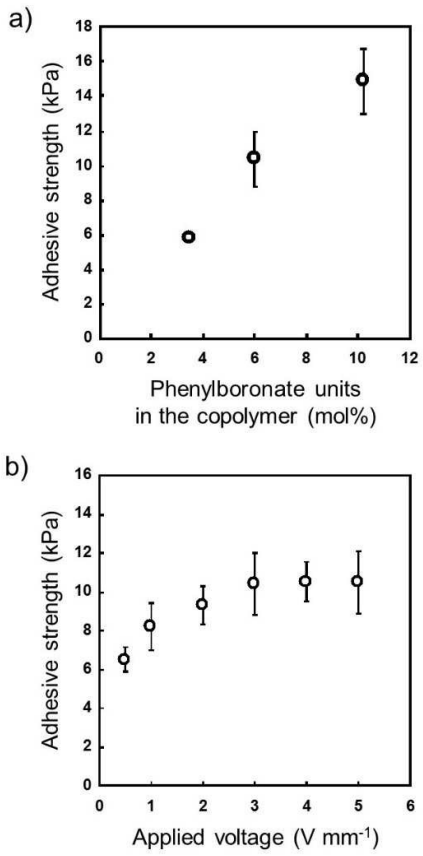

Fig. 3 (a) Adhesive strength of adhered PVA/PVA hydrogels as a function of phenylboronate units in the copolymers when adhesion was carried out by impression of 3 V mm^{-1} square wave (0.1 Hz) for 10 s. (b) Adhesive strength of PVA/PVA hydrogels as a function of applied voltage when the $PBA_{6.0}$ copolymer was used as binder. Electrophoresis condition was 0.1 Hz and 10 s. All PVA hydrogels were 20 wt% and data are expressed as the mean ± standard deviation (SD).

We investigated the stability of adhered PVA hydrogels under physiological conditions in the presence of sugar. Adhered gels (10 wt% PVA hydrogel and $PBA_{10.2}$ copolymer) were immersed in glucose, fructose, and sorbitol solution (PBS: pH=7.4, *I*=0.15) for 24 h at several concentrations at ambient temperature. The stability of adhered gels depended on sugar species and/or concentrations. Results are summarized in **Table 2**. In 0.01 mol L^{-1} sugar solution, adhered hydrogels were detached by sorbitol, although hydrogels broke without detachment in fructose and glucose solutions during a tensile test on both sides of the gels. It is reported that the association constant (K_{eq}) of ester formed with PBA of glucose, fructose, and sorbitol at pH=7.4 are 4.4, 160, and 370 L mol^{-1}, respectively.[35] Therefore, presence of sugars with larger K_{eq} value resulted in replacement of the sugar with a complex formed PVA to phenylboronate, and then detachment of adhered gels observed in a low concentration. When fructose was used as a competing agent, detachment of hydrogels was observed at 0.1 mol L^{-1}, and detached by glucose was observed as the concentration increased to 1.0 mol L^{-1}. Therefore, adherence of PVA hydrogels was stable without detachment under physiological conditions, but detachment was made possible by changing the sugar species and/or concentrations.

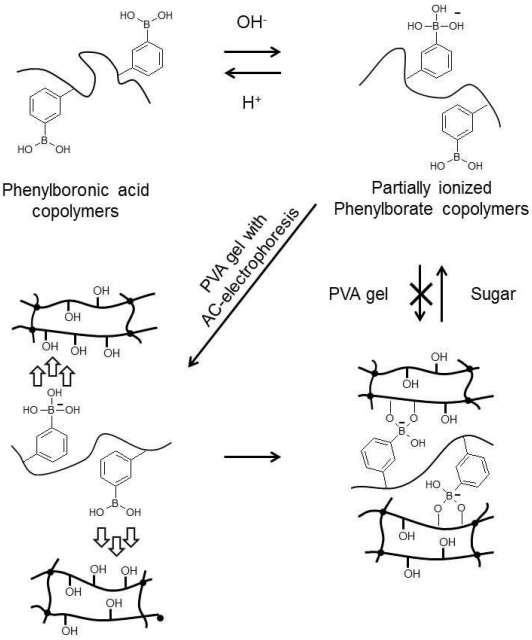

Fig. 4 Schematic illustration of AC electrophoretic adhesion of PVA hydrogels by manipulation of intermediate PBA copolymer under neutral conditions.

Table 2. Stability of adhered PVA/PVA hydrogels in the presence of sugar in PBS[a]

Concentration (mol L^{-1})	Glucose[b]	Fructose[b]	Sorbitol[b]
0.00	o	o	o
0.01	o	o	x
0.10	o	x	x
1.00	x	x	x

(a) 10wt% PVA hydrogels adhered to each other using $PBA_{6.0}$ copolymers. Hydrogels adhered to each other following a 3 V mm^{-1} with square wave (0.1 Hz) for 10 sec. (b) Hydrogels were (o) broken without detachment of the gels and (x) detached during a tensile test on both sides of the gels.

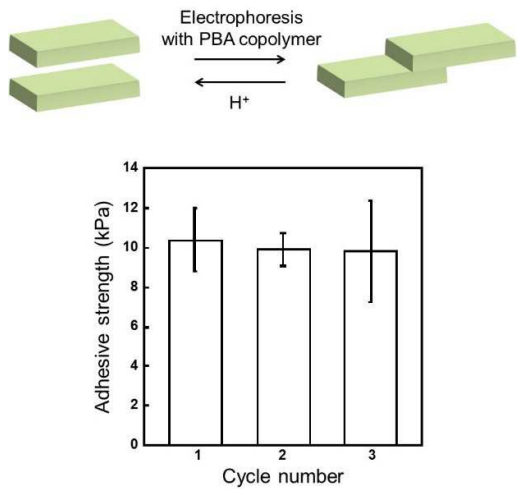

Fig. 5 Adhesive performance during repeated attachment and detachment cycles of 20 wt% PVA hydrogels with $PBA_{6.0}$ copolymers. Hydrogels adhered to each other following a 3 V mm^{-1} with square wave (0.1 Hz) for 10 sec. Data are expressed as the mean ± standard deviation (SD) (*n*=3).

We also investigated the reversible adhesion/detachment of 20 wt% PVA hydrogels. To examine the adhesive performance during repeated attachment and detachment cycles, two PVA hydrogels made adherent under AC voltage with $PBA_{6.0}$ copolymers and then detached by immersion in an acidic aqueous solution (**Fig. 5**). The same gels readily re-adhered under the same conditions. The initial adhesion strength was 10.4±1.6 kPa. As shown in **Fig. 5**, the adhesive strength of the re-adhered gels was 9.9±0.8 kPa and even after 3 cycles of adhesion/detachment, the adhesion strength was still 9.8±2.6 kPa. Since the adhesion strength remained relatively constant for at least 3 cycles, the results in **Fig. 5** suggest that adhesion of the hydrogels exhibits repeatability characteristics.

Conclusions

In conclusion, we manipulated water-soluble intermediate PBA copolymers to induce the rapid adherence of PVA hydrogels to each other using an AC electrophoresis technique. The PVA and PBA hydrogels were made to adhere during a DC electrophoresis. The adhesive strength of the hydrogels increased when increasing both the electrophoretic voltage and the amount of PBA units. The adhered PVA interface was stable under the physiological condition, but detachment was observed when sugar and acid were added in excess. Detached gels re-adhered under the same conditions, indicating that adhesion of the hydrogels exhibits repeatability characteristics. Electrophoretic adhesion of PVA and related hydrogels with PBA copolymer may be useful in the field of tissue engineering for the development of biocompatible and non-toxic 3-D soft materials.

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A table of contents

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