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Poly(vinyl alcohol) Hydrogel Can Autonomously Self-Heal

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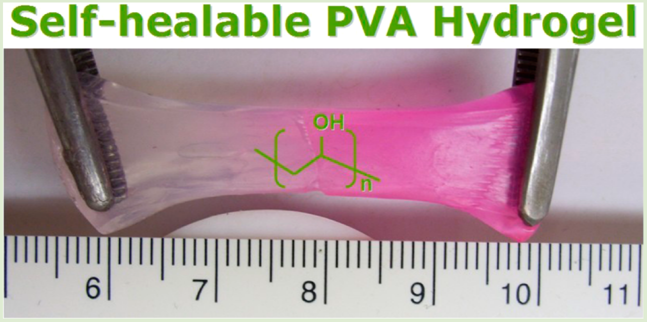
Supporting Information

ABSTRACT: It is discovered that poly(vinyl alcohol) (PVA) hydrogel prepared using the freezing/thawing method can self-repair at room temperature without the need for any stimulus or healing agent. The autonomous self-healing process can be fast for mechanically strong PVA hydrogel yielding a high fracture stress. Investigation on the effect of the hydrogel preparation conditions points out that hydrogen bonding between PVA chains across the interface of the cut surfaces is at the origin of the phenomenon. The key for an effective self-healing is to have an appropriate balance between high concentration of free hydroxyl groups on PVA chains on the cut surfaces prior to contact and sufficient PVA chain mobility in the hydrogel.



Self-healing materials possess the capability of repairing themselves after damages, which is a striking property that can prolong the lifetime of these materials and, thus, lower the cost. In recent years there is fast growing interest on a variety of self-healing polymers.[1−11] Of them, self-healing hydrogels have attracted much attention due to their great potential in biomedical applications.[12−24] It is no surprise to see that the main strategies for making self-healable hydrogels are all built up with the use of dynamic covalent bonds[16] or supramolecular interactions such as hydrogen bonding, electrostatic interaction, host−guest recognition, metal−ligand coordination, hydrophobic association, and π−π stacking.[17−24] Despite the exciting progress made on self-healing hydrogels, important challenges still remain. On the one hand, hydrogels for biomedical applications must have good biocompatibility and nontoxicity, whereas the designed self-healable hydrogels generally put the emphasis on their self-healing property without taking the biocompatibility and toxicity issues into great account. On the other hand, the current generation of self-healable supramolecular hydrogels generally suffers from low mechanical strength, which may be problematic for some biomedical applications such as tissue engineering scaffolds. Basically, the self-healing ability of a hydrogel is antagonist of its mechanical strength, because good polymer chain mobility, which favors chain diffusion across an interface of cut or fractured surfaces and predominantly influences the efficiency of self-healing, often means low mechanical strength of the hydrogel. It can also be noticed that many self-healing hydrogels are stimuli-healable hydrogels because their repairing process requires the input of a stimulus to be activated.[16,18,22−24]

Here we report the discovery that poly(vinyl alcohol) (PVA) hydrogel prepared under appropriate conditions can autonomously self-heal, exhibiting both good self-healing capability and mechanical strength. This finding is important because PVA hydrogel has been extensively studied and considered as one of the hydrogels the most suitable for biomedical applications due to its biocompatibility and nontoxicity.[25] The unveiled self-healing nature of PVA hydrogel adds a new appealing property to this old hydrogel and may hold promise for applications.

We prepared physically cross-linked PVA hydrogel using the well-known freezing/thawing method.[25] Typically, PVA (8 g, Mowiol 28−99 from Aldrich, MW: ~145000 g/mol, >99% hydrolysis) was dissolved in distilled water (22.8 mL) at ~95 °C under vigorous stirring; the homogeneous solution was then cast into a mold of desired dimension and cooled at −15 °C for 1 h, which was followed by thawing at room temperature for 12 h. Unless otherwise stated, the hydrogel used in this work was prepared at a PVA concentration of 35 wt % and subjected to one cycle of freezing/thawing, and for self-healing experiments, the cut pieces were brought into contact immediately after the cut (<5 s). The mechanical strength and appearance of the PVA hydrogel can easily be tuned by varying a number of parameters. Roughly, its mechanical strength and opacity are proportional to the concentration of PVA and the number of freezing/thawing cycles. For biomedical applications, physically cross-linked PVA hydrogel, being composed of only water and the polymer, compares advantageously with chemically cross-linked hydrogel that contains more chemicals (cross-linker, catalyst, etc.).[25] When the freezing/thawing method was used, crystallization of PVA occurs at low temperature resulting in the formation of crystallites that act as physical cross-links to

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hold the network structure in the PVA hydrogel.[25] Under our used experimental conditions, X-ray diffraction measurements found that the degree of crystallinity in the hydrogel containing 35 wt % of PVA is about 14% after one freezing/thawing cycle and 20% after three cycles (details on the characterizations of the hydrogel are given in Supporting Information). We found that such physically cross-linked PVA hydrogel can autonomously self-heal in air at room temperature without the need for any external stimulus or healing agent.

The phenomenon is shown with the pictures in Figure 1. Two pieces of original hydrogels, one of which contains a red pigment for visualization of the interface of cut surfaces, were prepared using 35 wt % PVA and one freezing/thawing cycle (Figure1a). They were cut into two pieces using scissors and two halves taken from each of the original hydrogels were put together rapidly to have their freshly created fracture surfaces brought into contact (Figure1b). A single piece of hydrogel emerged quickly from the two halves without any stimulus or healing agent; the diffusion of pigment molecules from one-half to the other could be noticed (Figure1c). After 12 h, while the cut region on the surface was still visible, the interface in the bulk disappeared almost completely; and the self-healed, one-piece hydrogel could withstand all kinds of mechanical forces without failure at the interface, such as bending (Figure 1d), twisting, compressing, and stretching to a large extension (Figure1e).

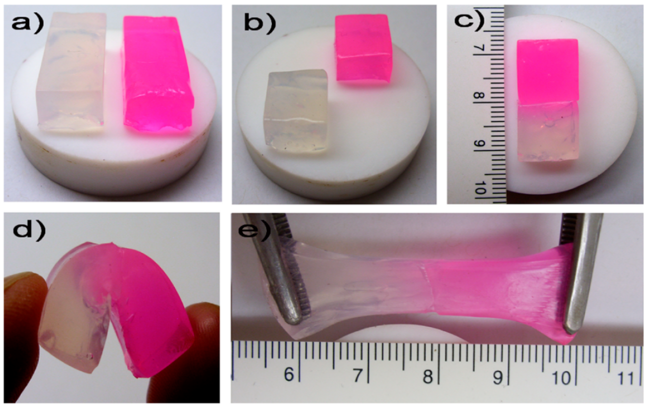

Figure 1. Photographs showing the self-healing behavior of PVA hydrogel: (a) two pieces of original hydrogel with and without rhodamine B for coloration; (b) two halves of the original hydrogels cut from the middle; (c) self-healed hydrogel upon bringing the two separate halves in contact for 12 h in air at room temperature without any external stimulus; (d) bending of the self-healed hydrogel; and (e) stretching of the self-healed hydrogel to about 100% extension.

To further quantitatively evaluate the self-healing property of the PVA hydrogel, tensile tests were performed on the original and self-healed samples with varying healing times. The results of one set of experiments are shown in Figure 2a. As expected, self-healed hydrogel samples ruptured at the interface upon elongation and the recoverable strength, denoted as fracture stress, increased with increasing the healing time. The fracture stress after 48 h healing is ~200 kPa, which is ~72% of the tensile strength of the original uncut hydrogel of the similar dimension and treated under identical conditions. To our knowledge, as far as autonomously self-healed hydrogels are concerned, the recovered fracture stress of ~200 kPa is the highest value reported up to now. It is also worth noting that more than half of the self-healing process occurred within the first hour after bringing the two pieces of cut hydrogel together. As seen in Figure 2a, after 1 h, the fracture stress has achieved ~105 kPa, corresponding to ~40% of the initial tensile strength recorded with the uncut sample. Similarly, after 10 min self-healing, the fracture stress was already up to an impressive ~60 kPa. Actually, the hydrogel self-healed for less than 10 s could withstand a stress around 10 kPa, which may be a very meaningful mechanical strength for certain hydrogel applications. These results indicate the occurrence of a very rapid and efficient autonomous self-healing process in such physically cross-linked PVA hydrogels. Figure 2b shows the plot of the fracture stress recovery, averaged over the results of several sets of experiments, versus the healing time, further illustrating the fast occurring self-healing within the first hour after putting the cut surfaces together. It can be noted in Figure 2a that prior to their failure at the interface the self-healed samples display slightly higher stresses than the uncut hydrogel upon elongation. While this apparent difference may be partly attributed to experimental uncertainty in the measurements, it may be indicative of small changes in the toughness of the self-healed hydrogel, which could be caused by the loss of some water molecules during the specimen manipulation required for the self-healing experiment. Apart from the tensile test, the repeatability of the hydrogel's self-healing ability was also investigated. It was found that the PVA hydrogel could experience many cycles (>10) of damage and healing along the interface with the fracture stress decreased slightly over the cycles (data of 10 cycles of tests are shown in Figure S1).

Considering the hydroxyl group of vinyl alcohol, the autonomous self-healing ability of the PVA hydrogel is likely to stem from the formation of hydrogen bonding between PVA

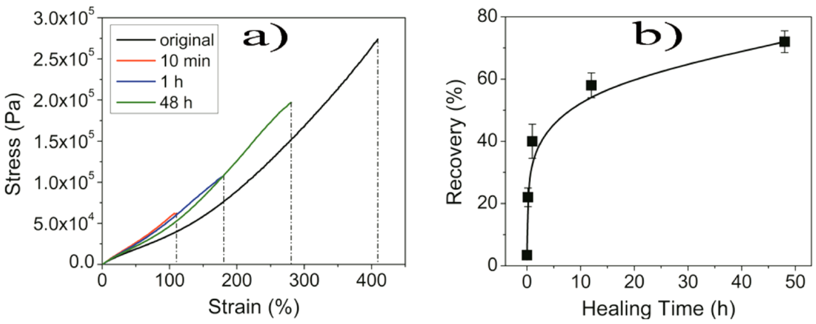

Figure 2. (a) Stress−strain curves of original and self-healed PVA hydrogel at various healing times (35% polymer) recorded at room temperature under a tensile rate of 1 mm/s. (b) Plot of the recovery of tensile strength (fracture stress) of self-healed hydrogel vs healing time. Error bars denote the standard deviations from at least three experiments.

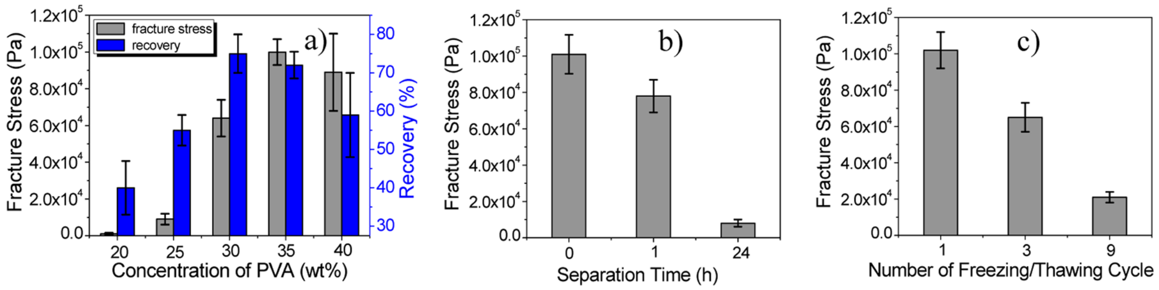

Figure 3. Effect of the preparation conditions of PVA hydrogel on their fracture stress after self-healing at room temperature: (a) PVA concentration in the gel; (b) separation time before bringing two cut surfaces into contact for self-healing (35% PVA); and (c) number of freezing/thawing cycles (35% of PVA). Error bars denote the standard deviations from at least three experiments.

chains. It is easy to picture that the hydrogen bonds contributing to the self-healing should essentially be those formed between PVA chains on both sides of the interface and/or those between PVA chains on one side and PVA chains diffusing across the interface from the other side when the two cut surfaces are brought into contact. To get more insight into the underlying mechanism, we investigated the impact of a number of parameters on the self-healing efficiency, including the concentration of PVA in the gel, the separation time of the cut hydrogel before being brought into contact and the number of freezing/thawing cycles. The results in Figure 3 show that all the parameters affect profoundly the self-healing ability of the PVA hydrogel. Overall, what favors the formation of intermolecular hydrogen bonding between PVA chains and the diffusion of PVA chains across the interface strengthens the self-healing process. First, the concentration of PVA in the hydrogel plays an important role (Figure 3a). Up to 35 wt %, the fracture stress of self-healed PVA hydrogel increases sharply with increasing the polymer content while keeping other conditions the same. The hydrogel cannot repair itself if the concentration of PVA is below 20 wt % regardless of the healing time and number of freezing/thawing cycles. This result implies that a sufficient amount of polymer chains on the cut surfaces is necessary to promote a sufficient number of H-bonds formed between PVA chains across the interface. At a low concentration of <20 wt %, PVA chains are well dispersed and surrounded by water molecules so that the chance for PVA chains on the two sides to reach each other to form H-bonds can be severely diminished. However, when the concentration of PVA is higher than 35 wt %, the recovered fracture stress goes down. At 40 wt % of PVA, it became difficult to obtain a homogeneous solution due to some insoluble polymer. Also reported in Figure 3a is the healing efficiency (after 48 h healing) in terms of recovered fracture stress with respect to the original uncut hydrogel. The most effective recovery was found for hydrogels with a PVA concentration of 30−35 wt %. Altogether, with the used molecular weight of PVA, the optimal polymer concentration is about 35 wt %.

Second, at 35 wt % of PVA, the fracture stress of self-healed PVA hydrogel decreases drastically with increasing the separation time before putting the cut surfaces together (Figure 3b). While most of the hydrogel's self-healing ability remains at a separation time less than 1 h, the hydrogel loses almost completely its self-healing ability after 24 h or longer separation. This result is no surprise and suggests that, after cutting the hydrogel, if the two new surfaces are kept separated from each other, PVA chains on the same surface could rearrange to allow their hydroxyl groups to form either interchain or intrachain H-bonds to minimize the surface energy. The consequence of this is that the number of free hydroxyl groups on each surface decreases over time, which reduces the number of H-bonds that can be formed across the interface when the two surfaces are brought together.[4,17] In an attempt to observe the temporal evolution of the numbers of free and H-bonded hydroxyl groups of PVA on a cut hydrogel surface, we recorded infrared spectra of a freshly cut surface and after various separation times. Unfortunately, no information could be extracted due to the dominant absorption bands of H-bonded water molecules in the 3000−3500 cm^{-1} spectral region hiding the absorption bands of PVA (Figure S2).

Third, at 35 wt % of PVA, the number of freezing/thawing cycles also impacts the hydrogel's self-healing ability (Figure 3c). The hydrogel prepared using this method is known to become harder and more opaque with increasing the number of freezing/thawing cycles as a result of increased crystallinity of PVA chains.[26,27] X-ray diffraction and viscoelastic measurements on our hydrogels confirmed an increased crystallinity and mechanical strength with increasing the number of freezing/thawing cycles (Figures S3 and S4). Generally, a greater hardness of hydrogel means reduced chain mobility. If polymer chains on the two surfaces cannot migrate or diffuse from one side to the other due to the lack of chain mobility, obviously the self-healing process cannot develop effectively. This explains the decreasing fracture stress of self-healed hydrogel with increasing the number of freezing/thawing cycles. Furthermore, there are other parameters that can affect the self-healing behavior. For instance, with one freezing/thawing cycle, different freezing times could also affect the self-healing performance. Again, the optimal conditions (PVA concentration, number of freezing/thawing cycles, freezing time, separation time, etc.) could vary for PVA samples having different characteristics and thus different crystallization kinetics in the formation of the physically cross-linked state. From all of the above results, the key to a fast and efficient autonomous self-healing of hard PVA gel appears to have enough free hydroxyl groups on the cut surfaces susceptible to form H-bonds across the interface (determined by PVA concentration and separation time of cut surfaces) and yet a sufficient chain mobility that is required for chain diffusion across the interface and association of hydroxyl groups to form H-bonds (determined by the number of freezing/thawing cycles and freezing time).

As mentioned above, the gelation of PVA dissolved in water upon the freezing/thawing cycle is due to partial crystallization of PVA chains that results in hard crystallites serving as physical cross-links of a network structure. When a hydrogel is cut into two pieces, the possibility of having broken crystallites on the cut surfaces cannot be ruled out. As the cut surfaces are brought into contact, it would also be possible that crystallization of PVA chains at the interface occur over time and contribute to the self-healing. At this point, we have no experimental evidence to support this hypothesis. However, crystallization of PVA at the interface is unlikely under our used experimental conditions. Indeed, all self-healing tests were carried out at room temperature (~25 °C), while the crystallization of PVA in the hydrogel occurs at much lower (subambient or freezing) temperatures.[25]

In summary, we reported the finding that physically cross-linked PVA hydrogel prepared using the freezing/thawing method can autonomously self-heal at room temperature without the need for any stimulus or healing agent. The self-healable hydrogel can be mechanically strong exhibiting the highest fracture stress reported so far. Our studies suggest that the key to obtaining fast and efficient self-healing of mechanically tough PVA hydrogel is to have a good balance between a sufficient amount of free hydroxyl groups of PVA on cut surfaces required for forming interchain H-bonds and enough chain mobility ensuring chain diffusion across the interface. The discovery is important because PVA hydrogel is low cost, easy to produce, and has great potential for biomedical applications due to its biocompatibility and nontoxicity. The discovered self-healing ability adds a new value to this old hydrogel.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Experimental details and more hydrogel characterization results, including data obtained with WAXD, ATR, DMTA, and tensile test. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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