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Self-Healing Polymer-Clay Hybrids by Facile Complexation of a Waterborne Polymer with a Clay

Aranee (Pleng) Teepakakorn and Makoto Ogawa

Water-induced self-healing materials were prepared by the hybridization of a water-soluble polymer, poly(vinyl alcohol), with a smectite clay by mixing in an aqueous media and subsequent casting. Without using chemical crosslinking agent or heat treatment, the poly(vinyl alcohol)-clay hybrid was adhered strongly on the substrate to show self-healing when immersing in water (25°C). The healing was completed within 1 min by soaking a damaged poly(vinyl alcohol)-clay film under such conditions as in cold water (2°C), simulated seawater, steam, HCl solution (pH=1) and NaOH solution (pH=14). The healing was seen repeatedly for 10 times.

Introduction

The protection of the materials’ surface from being damaged by external mechanical forces is one of the important requirements for sustainable uses of materials, so that the materials covered by the protective layers which has mechanical toughness and healing ability have been investigated. Self-healing coating is a capability of a protective layers to recover its damages involving the rupture of chemical and/or physical bonds. Among the materials showing healing phenomena, self-healing polymers have been investigated extensively for various applications as energy storage/conversion devices, electronic medical devices, adhesion to the solid substrate and eco-friendly preparation method are expected in addition to the healing performances. Materials with healing ability under various conditions are also worth developing.

As an alternative ecofriendly stimulus, self-healing polymer in water has been studied and used as a protecting layers for civil engineering products, biomaterials and electronic devices in not only an ambient condition but also underwater applications. Water is used to facilitate the reversible molecular interactions/bonds between the functional groups on the polymer backbone. A variety of polymers has been designed for water-induced self-healing, for example catechol-functionalized polymers with or without complexation with polymer based boronic ester, poly(vinylidene fluoride-co-hexafluoropropylene), an assembly of cationic and/or anionic polymers, and nonionic water-soluble polymers. In order to “insolubilize” water-soluble polymers and to achieve mechanical strength and chemical stability, such methods as the addition of chemical crosslinking agent, heat treatment and introduction of nanofiller are known. For the practical use of self-healing materials, mechanical strength, chemical stability, adhesion to the solid substrate and eco-friendly preparation method are expected in addition to the healing performances. Materials with healing ability under various conditions are also worth developing.

Addition of nanofillers has been used to modify the properties of various polymers. Smectite, which is a group of layered clay mineral with 2:1 type phyllosilicate structure, is one of the nanosheet fillers used extensively as polymer additives. The interactions with smectites and the properties of the resulting polymer-clay hybrids have been investigated for various polymers including water-soluble ones. The in-situ polymerization of acrylamide in the presence of a smectite was reported to obtain the hydrogel (named as NC gel), which showed the mechanical robustness, stability in water and self-healing property. In the present study, a hybrid of a water soluble polymer, poly(vinyl alcohol), and a smectite clay is prepared to obtain a coating, which shows self-healing behavior under varied conditions. The polymer-clay composition is shown to be a key parameter to control the solubility of water-soluble polymer, degree of swelling, and self-healing of the resulting product.
Experimental section

Materials
Poly(vinyl alcohol) (abbreviated as PVA; n = 2,000), rhodamine 6G (abbreviated as R6G) and sodium chloride (abbreviated as NaCl) were purchased from Tokyo Chemical Industry Co., Ltd. from Japan. A synthetic hectorite (Sumecton SWF, abbreviated as SWF, the cation exchange capacity (CEC) of 70 mmol/100g) was donated from Kunimine Ind. Co. Ltd., Japan. Sodium hydroxide (abbreviated as NaOH, pellets ≥ 98% purity) was purchased from Sigma-Aldrich from USA. Hydrochloric acid (abbreviated as HCl, 37%) was obtained from Merck KGaA from Germany. All the chemicals were used without further purification. Water was purified by a Milli-Q system (18 MΩ cm⁻¹, Millipore) before the uses. Microscope borosilicate glass slides were obtained from BRAND GMBH + Co. Kg from Germany.

Sample Preparation
SWF (2.25, 1.23 0.85, 0.43 and 0.36 g for the weight ratios of PVA/SWF = 0.36, 1.08, 1.80, 4 and 5, respectively) was dispersed in 160 ml of DI water by magnetic stirring for 1 day. R6G (1mmol/100g clay) was mixed with SWF suspension in order to stain the samples for naked eye observations. Then, an aqueous PVA solution (40 ml) was added to the R6G-SWF suspension. The amount of PVA was 0.81, 1.33, 1.53, 1.74 and 1.78 g, which corresponded to the weight ratios of PVA/SWF = 0.36, 1.08, 1.80, 4 and 5, respectively. The mixture was magnetically stirred for another 1 day to obtain homogeneous suspension. The aqueous suspension of SWF and the PVA solution containing 1 mmol/100 g R6G were also prepared as references. Before casting, all the suspensions were sonicated for 30 min to eliminate air bubbles. Borosilicate glass substrate (12 x 25 mm) was cleaned with an aqueous solution of NaOH (pH 10-11) for 1-2 day at room temperature and dried in air. An aliquot (250 µl) of the PVA-SWF suspensions (weight ratio of PVA/SWF = 0.36, 1.08, 1.80, 4 and 5; the samples were designated as 0.36 PVA-SWF, 1.08 PVA-SWF, 1.80 PVA-SWF, 4 PVA-SWF and 5 PVA-SWF), SWF suspension or PVA solution were casted on the glass substrate using micropipette and dried in air. An aliquot (250 µl) of the PVA-SWF suspensions were casted on the glass substrate in order to stain the samples for naked eye observations. Then, an aqueous PVA solution (40 ml) was added to the R6G-SWF suspension. The amount of PVA was 0.81, 1.33, 1.53, 1.74 and 1.78 g, which corresponded to the weight ratios of PVA/SWF = 0.36, 1.08, 1.80, 4 and 5, respectively. The mixture was magnetically stirred for another 1 day to obtain homogeneous suspension. The aqueous suspension of SWF and the PVA solution containing 1 mmol/100 g R6G were also prepared as references. Before casting, all the suspensions were sonicated for 30 min to eliminate air bubbles. Borosilicate glass substrate (12 x 25 mm) was cleaned with an aqueous solution of NaOH (pH 10-11) for 1-2 day at room temperature and dried in air. An aliquot (250 µl) of the PVA-SWF suspensions (weight ratio of PVA/SWF = 0.36, 1.08, 1.80, 4 and 5; the samples were designated as 0.36 PVA-SWF, 1.08 PVA-SWF, 1.80 PVA-SWF, 4 PVA-SWF and 5 PVA-SWF), SWF suspension or PVA solution were casted on the glass substrate using micropipette and dried at a constant temperature (25-26°C) and humidity (70-80 %RH) in a plastic closed box with the dimension of 24“x14“x18.5” for the slow evaporation of water to achieve uniform distribution and the orientation of clay particles parallel to the substrate. The film thickness was determined using a surface profilometer (Dektak XT, Bruker) to be 4.9 ± 0.8, 4.8 ± 0.8, 5.0 ± 0.9, 5.2 ± 0.1 and 5.2 ± 0.2 µm for 0.36, 1.08, 1.80, 4 and 5 PVA-SWF, respectively. The depth profile along the length of the engraved 0.36, 1.08, 1.80, 4 and 5 PVA-SWF films is shown in Figure S6. Two ridges formed along the engraved part as seen in all the temporal evolution plots. These two ridges were not taking into account for the thickness measurement.

Healing test
Films were engraved by scalpel and the size of the notch was approximately 30 µm. The engraved film was healed by immersing the samples into water (R.T.), cold water (2°C), simulated sea water (0.6 M NaCl solution), acidic solution (HCl pH=1), basic solution (NaOH pH=14), steam and a hydrothermal condition (heating at 100°C under 80 kPa in a kitchen cooker for 2 h).

Adhesion test
The 1.80 PVA-SWF suspension was casted on the stainless-steel hook and dried at room temperature (Figure S4A and D). Water was sprayed to the film and attached to both glass and frosted glass windows (Video S1 and S2). The hook that attached to the glass and frosted glass was hold for 24 h before hanging 500 g of iron balls.

Shear lap test
The lap shear strength was evaluated using the tensile tester (ADMET eXpert 5604, load cell 50 LB) as shown in Figure S8. 0.36 and 1.80 PVA-SWF suspensions were casted on the glass substrate with the size of 2.5 x 2.5 cm. The thickness of 0.36 and 1.80 PVA-SWF films were about 10 µm. A polypropylene sheet was used as cover the sample at a grip site. Water was sprayed to the sample, then, uncoated glass plate was attached and hold for 24 h. The adhesion was evaluated by the tensile strength testing with the loading rate of 2 mm/min. The measurement was repeated for 3 times.

Characterization
X-Ray diffraction patterns were recorded on a diffractometer (Bruker New D8 Advance equipped with Ni filtered Cu Kα radiation). Scanning electron micrographs (SEM) were obtained on a JEOL JSM-7610F field-emission scanning electron microscopy instrument. Prior to the measurements, the samples were coated with platinum with the thickness of 10-12 nm. Elemental mapping images were obtained on an Oxford energy dispersive X-ray fluorescence spectrometer (X-Max 150 mm²) equipped with SEM (JEOL, JSM7610F). The healing was followed by a microscope (Senterra II, R200-532, Bruker) with a 4× microscope magnification at 25°C. The damage depth of the scratched films was evaluated using a profilometer (Dektak XT, Bruker) with a 2 µm radius stylus and stylus force of 0.01 mN.

![Figure 1. XRD patterns of 0.36 PVA-SWF (a,b), 1.08 PVA-SWF (c,d) and 1.80 PVA-SWF (e,f) film before (black) and after (red) the soaking in water for 24 h.](image)
Results and discussion

By the simple casting of the suspension containing PVA and SWF on the glass substrate, coating of PVA-SWF hybrids was obtained. The XRD patterns of the PVA-SWF films are shown in Figure 1. The basal spacing (d001), which was determined by Bragg’s equation from the reflection at the lowest 2 theta region, was larger with the PVA content as 1.63, 2.70 and 4.09 nm for 0.36, 1.08 and 1.80 PVA-SWFs, respectively. Systematic variation of the interlayer expansion of smectites depending on the amount of the added polymers (poly(vinyl pyrrolidone) or PVP and PVA) was reported. PVA was thought to be preferentially intercalated into the interlayer space of SWF. The interlayer volume of the PVA intercalated SWF was calculated from the composition, the ideal surface area of smectites (750 m²/g clay) and the observed gallery height, which was obtained by subtracting the thickness of the silicate layer (1 nm) from the observed basal spacings (d001), to be 2.4×10⁷, 6.4×10⁷ and 1.2×10⁸ m³/g clay for 0.36, 1.08 and 1.80 PVA-SWFs, respectively. From the interlayer volume and the composition, the density of PVA was estimated to be 1.5-1.6 g/cm³, which is slightly higher than bulk density of PVA (1.01 g/cm³). The difference is thought to be due to the hydration of the interlayer space, the adsorption of PVA at the external surface of the clay particles and the dense packing of PVA chain in the interlayer space of SWF. The reflection due to the basal spacing was not clearly seen when the weight ratio of PVA-SWF was higher than 4 (Figure S1), suggesting the further expansion of the interlayer space, which was not detectable by the present measurement.

The photographs of the films before and after the soaking in water for 24 h are shown in Figure 2. By the soaking, PVA was dissolved and SWF was dispersed into water, resulting in the disappearance of the pure PVA and SWF samples from the substrate. Some part of 4 and 5 PVA-SWF films was swollen in water, resulting in the partial liberation from the substrate as shown in Figure 2, which was supported by the weight loss of the film after the soaking (Table S1). On the contrary, 0.36, 1.08 and 1.80 PVA-SWF films were adhered to the substrate as shown by the appearance of the films (Figure 2, no significant change was seen after the immersion). No weight loss/gain was observed upon the soaking (Table S1) and the basal spacing did not change (Figure 1), confirming that 0.36, 1.08 and 1.80 PVA-SWFs were stably adhered to the substrate without swelling. For the oxygen and water vapor barrier film obtained by the hybridization of PVA with smectites, the low oxygen and water vapor permeation was explained as a result of the tortuous path by the parallel orientation of clay platelets in PVA matrix and hydrogen bonding between PVA and clay surface. It was found that the diffusion of water and oxygen decreased as the volume fraction of clay in the hybrid increased. In the present study, water permeation was thought to be restricted for PVA-SWFs with lower PVA contents, supporting the observed difference in the insolubilization depending on the composition.

Possible roles of smectite as a crosslinker was proposed for the hydrogels prepared by the in-situ polymerization of poly(N-isopropylacrylamide) and poly(N,N-dimethylacrylamide) and freeze thawing of PVA in the presence of smectite and organically modified smectite, respectively. In these studies, the clay content was within 2-25 wt%, where possible exfoliation of clay in the polymers was proposed. On the other hand, PVA was intercalated into the interlayer space of smectite.
for 0.36, 1.08, and 1.80 PVA-SWFs as shown by the expansion of the interlayer space derived from the XRD results. The stability of PVA-SWF hybrids in water was thought to be due to the ion-dipole interactions and hydrogen bonding between the hydroxyl group along the PVA chain to the silicate surface as well as the intermolecular hydrogen bonding between the PVA in addition to the restricted water permeation through “torturous path” as discussed before.

The orientation of the silicate layers parallel to the substrate was seen in the SEM images of the cross-section of the 1.80 PVA-SWF film (Figure 3A-C). The film surface was smooth, and the thickness was 4.3 µm which was in agreement with the depth profile analysis by profilometer (Figure 56). The silicate nanosheet with the thickness of 1 nm was not seen clearly from the SEM analysis even at the magnification of 150 k (Figure 3B) due to the small particle size of SWF (SEM image of SWF is shown in Figure S7). The uniform distribution of SWF platy particles from the bottom to the surface of the film was due to the small particle size of SWF (SEM image of SWF is suggested for 1.80 PVA-SWF from the layered texture of the film cross section, while the layered texture was not visible for 4 PVA-SWF film (Figure 3D). This difference is consistent with the XRD results, where diffraction from the basal plane of SWF was seen for 1.80 PVA-SWF and not seen for 4 PVA-SWF film. The structural image of 1.80 PVA-SWF is shown in Figure 3F. The thickness can be varied by using different amount of the suspension as well as by changing the concentration of the suspension. Figure 3C shows the SEM images of 1.80 PVA-SWF with the thickness of 25 µm. In the hybridization of a clay with sodium polyacrylate, the phase separation of the polymer from the precipitated clay was found when the amount of polymer was 30 wt%51. Such phase separation was not seen for 1.80 PVA-SWF (the amount of polymer was 64 wt%), which is an important positive aspect of the present study to achieve homogeneous dispersion of clay particle through the film.

Thanks to the homogeneity of the suspension, other coating techniques are also feasible for the preparation of PVA-clay films with varied thickness and shape on various substrates.

Water-induced self-healing of 1.80 PVA-SWF film was investigated by immersing the engraved film with the thickness of 5.0 ± 0.9 µm in water at room temperature (Figure 4A). Elemental analysis of the engraved and healed films (Figure 4B) indicated that both PVA and SWF attended the recovery. The mechanical damage generated the interfacial regions which the interface polymer chain exhibited higher degree of freedom compared to the bulk region52,53. Water was used to facilitate the diffusion of PVA across the cut region for regeneration of the hydrogen bonding between PVA chain and smectite surface and PVA chain itself. The SWF nanosheet did not restrict the diffusion of PVA but SWF and PVA were diffused together to complete the healing as indicated in the elemental mapping of the scratched/healed part (Figure 4B). The evolution of the depth along the length of the surface’s defect was characterized by profilometer (Figure 4C). A small ridge with the height of 7 µm was presented at the healed surface. It may be due to 2 possible reasons 1) the diffusion rate of PVA at the middle of the interlayer space was different from PVA absorbed at the surface of SWF and 2) the healing was achieved within 1 min, so longer time is required for the full recovery. Nevertheless, the re-healing by scratching the film at the same area and the subsequent exposure in water for 1 min was seen for 10 times (Figure S2). The self-healing of PVA-SWF hybrid was shown in various aqueous conditions as cold water (2°C), steam, sea water, acid solution (HCl pH=1) and basic solution (NaOH pH=14) as shown by the photographs (Figure 5).

The effects of the film thickness on the healing property were studied and the results are summarized in Figure S3. No healing was observed when the thickness of the film was 1 µm. The heating of the 1.80 PVA-SWF with the thickness of 2 µm was present after the immersion in water for 30 min while healing was not completed by prolong the immersion time to 24 h. The limitation of healing is explained as the adhesion of PVA-SWF hybrid film with the hydrophilic surface of the glass substrate. Thus, the driving mechanism for PVA-SWF self-healing is the competition between the interactions of PVA-SWF with water and PVA-SWF with glass substrate. The effect of the film

Figure 4. Microscopy images (A), SEM images and elemental mapping data (B) and temporal evolution of the depth along the length (C) of engraved and healed 1.80 PVA-SWF film by immersion in water for 1 min.

Figure 5. Microscopy images of engraved and healed 1.80 PVA-SWF films by immersion in HCl solution (pH=1), NaOH solution (pH=14), simulated sea water (0.6 M NaCl solution), cold water and steam for 1 min.
thickness to the self-healing was reported for the PVP coated with aminoethyl-functionalized layered magnesium silicate, where the film with the thickness over 100 nm was required for the complete healing. Further systematic studies on the healing behavior of the present hybrid as supported films on various substrate as well as free standing films are also worth investigating.

Reported examples of water-induced self-healing polymer coating are summarized in Table 1. Layer-by-layer (LbL) assembly technique has been used to prepare water-induced self-healing materials. Uniform stacking of oppositely charged materials have been obtained by sequential deposition, while it is difficult and time consuming to produce the thick film by the LbL technique. In the present study, simple casting was employed because the method is simple, ecofriendly and environmentally friendly technique to obtain uniform polymer-clay film. There is no polymer or clay loss during the film fabrication and the film thickness is easily adjusted by the volume and the concentration of the suspension containing polymer and clay, which are the additional advantages of the casting method. In addition to the improvement of the mechanical robustness of polymer through the interactions with the added particles, a chemical crosslinking agent and/or heat treatment is required for the stabilization of nonionic polymers in water as polyethylene dioxythiophene (PEDOT) doped with poly styrene sulfonate (PSS) (PEDOT:PSS), poly(ethylene glycol) (PEG) and PVA. Even though the addition of chemical crosslink agent and any thermal treatment were not employed for the insolubilization of PVA, the present 1.80 PVA-SWF hybrid film was stable in water for more than 24 h. If compared with the previous reports on water induced self-

| Polymer  | Filler/ content | Crosslinking agent | Method               | Film Thickness | Cut size | Healed condition          | Re-healing | Ref |
|----------|----------------|--------------------|----------------------|----------------|---------|---------------------------|-----------|-----|
| PEI-PAA  | -              | hyaluronic acid    | Layer-by-layer       | 34 µm          | 50 µm   | in water 5 min            | 5 times    | 24  |
|          |                |                    | technique            | 700 nm         | 0.2 µm  | 97% RH 10 min             | -         | 55  |
|          |                |                    |                      | 700 nm         | 4.8 µm  | in water 24 h and left 24 h | -         | 56  |
|          |                |                    |                      | 29 µm          | 29 µm   | in water 26-34 min        | 5 times    | 57  |
|          |                |                    |                      | 58.8 µm        | 48 µm   | drop 0.1 ml water 5 min   | -         | 58  |
| b-PEI-PAA| -              |                    |                      |                |         |                           |           |     |
|          |                |                    |                      | 20 µm          | 4.3 µm  | in water 30 min           | 20 times   | 59  |
|          |                |                    |                      | 25 µm          | 76 µm   | in water 10 min           | -         | 60  |
|          |                |                    |                      | 32 µm          | 80 µm   | in water 30 min           | 5 times    | 61  |
| PEDOT-PSS| -              | heat 80, 110 and 140°C | casting             | 1 µm          | 44 µm   | drop 10 µL water 150 ms   | -         | 62  |
| PVP      | AMP-Clay/      | spin coating       |                      | 900 nm         | 20-30 µm| ≥ 50% RH 36 h             | -         | 27  |
| PFOS- PVP| 20 wt%         | spray coating      |                      | 100 nm         | 10 µm   | ≥ 80% RH 24 h             | -         | 28  |
| PEG      | tannic acid    | casting            |                      | 46.5 µm        | 50 µm   | in water 5 min            | 5 times    | 25  |
| PVA      | Nafion/ 15 wt% | dip coating        |                      | 29 µm          | 125 µm  | in water 20 min           | 5 times    | 30  |
|          | GO/ <10 wt%    | Layer-by-layer     |                      | 42 µm          | 50 µm   | in water 30 min           | 20-30 times| 31  |
|          | Clay/ <20 wt%  | tannic acid        | doctor blade         | 42 µm          | 50 µm   | in water 30 min           | 6-12 times | 32  |
|          | Clay/ 35-74 wt%| -                  | casting              | 5 µm           | 30 µm   | in water, HCl, NaOH, steam, NaCl, cold water 1 min | more than 10 times | This work |

Abbreviations; PEIs = poly(ethyleneimine), bPEIs = branched polyethyleneimine, PAA = poly(acrylic acid), PEDOT-PSS = polypentaerythritol phosphate doped with polystyrene sulfonate, PVP = polyvinylpyrrolidone, PEG = polyethylene glycol, PFOS = perfluorooctanesulfonic acid potassium salt, GO = Graphene oxide, AMP-clay = aminopropyl-functionalized layered magnesium silicate.
healing polymers (summarized in Table 1), the present PVA-SWF hybrid has such advantageous aspects as simple preparation, the products’ stability in water and the fast response of the healing, repeatable healing and able to heal under various conditions as cold water (2°C), steam, simulated sea water (0.6 M NaCl solution), acidic solution (HCl, pH=1) and basic solution (NaOH, pH=14). On the other hand, the film was liberated from the substrate by a hydrothermal treatment at 100°C 80 kPa for 2 h, which is a next challenge of the present material design. PVA-SWF hybrid is a possible candidate to be used as a water-based protective coating of material not only from the mechanical damage but also environmental exposure (O2 and H2O). Such different coating method as doctor blading, spray coating and dip coating are applicable. On the other hand, the adhesion of the coating should be evaluated before the application, so that the study on the coating of the hybrids on various substrates are worth investigating.

The adhesion of the 1.80 PVA-SWF to the substrate was further confirmed by the fabrication of the hybrid as a hook’s adhesive. The thicknesses of 15 and 45 µm were required for the attachment of hook on the glass and frosted glass (surface roughness of 14±2 µm), respectively. By using the thickness of 45 µm, the hook that attached to the glass and frosted glass could hang 500 g of iron balls for more than 24 h (Figure S4B and E). After that, the hooks were pull out from the glass and frosted glass windows (Video S3 and S4). There are no PVA-SWF film remaining on the windows while the surface roughness of the film changed after the attachment to the frosted glass (Figure S4C and F). The surface roughness of the film before and after attachment to frosted glass was evaluated by profilometer (Figure S5). The roughness of film was increased from 0.9±0.2 µm to 8±2 µm indicating the softness property of PVA-SWF surface. This experiment indicated the flexibility of the PVA-SWF film upon the mechanical compressing (manual compressing) to adjust the shape to some extent for better adhesion. These observations suggested the importance of the thickness of the coating to be adhered to the substrates with varied surface roughness. In other words, the strength of the adhesion could be varied by the roughness of the surface to be attached. In addition, the effect of composition on the adhesion was evaluated using tensile tester (shear lap test). The relationship between shear load and the displacement is shown in Figure S9. The average shear strength for the separation of the plates was 105.9 ± 11.9 and 38.9 ± 4.2 kPa for 0.36 and 1.80 PVA-SWFs, respectively. Adhesion of the present hybrids to various substrates and under different conditions is being investigated in our laboratory to clarify possible application of the present films.

Conclusions

Water-induced self-healing hybrid was designed from a water-soluble polymer, poly(vinyl alcohol), with a smectite clay. The preparation was based on a simple mixing of the components in an aqueous media and subsequent casting on the glass substrate. The sedimentation induced the orientation of PVA intercalated SWF platy particles parallel to the substrate. The poly(vinyl alcohol)-clay hybrid film under various condition as water (25°C), cold water (2°C), HCl solution (pH=1), NaOH solution (pH=14), steam, and NaCl seawater within 1 min. The damage-healing cycle was repeated for 10 times.

Conflicts of interest

There are no conflicts to declare.

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