Semi-IPNs with Moisture-Triggered Shape Memory and Self-Healing Properties

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Moisture or water has the advantages of being green, inexpensive, and moderate. However, it is challenging to endow water-induced shape memory property and self-healing capability to one single polymer because of the conflicting structural requirement of the two types of materials. In this study, this problem is solved through introducing two kinds of supramolecular interactions into semi-interpenetrating polymer networks (semi-IPNs). The hydrogen bonds function as water-sensitive switches, making the materials show moisture-induced shape memory effect. The host–guest interactions (β-cyclodextrin-adamantane) serve as both permanent phases and self-healing motifs, enabling further increased chain mobility at the cracks and self-healing function. In addition, these polyvinylpyrrolidone/poly(hydroxyethyl methacrylate-co-butyl acrylate) semi-IPNs also show thermosensitive triple-shape memory effect.

1. Introduction

Self-healing materials (SHMs) are a type of biomimetic intelligent materials that possess the ability of self-healing and regeneration of functions from a physical damage. Over the past decade, SHMs have attracted increasing attention because they offer enormous possibilities to improve the reliability and safety of man-made materials. Encouraging progress in the field of SHMs has been achieved. New design strategies and various self-healing species have been explored. However, in many practical applications, fracture surfaces cannot autonomously come together into needed closure for healing close proximity. Addressing this problem, a new concept that uses shape memory effect to assist the self-healing process has been explored. Shape memory polymers (SMPs) are another kind of significant intelligent material that has the capability of changing from a temporary shape to a permanent shape when subjected to external stimuli (like pH, heat, water, light, redox agents, etc.). The stimuli-responsive nature of SMPs enables them to have a wide range of potential applications ranging from sensors to biological and biomedical engineering. In 2008, Manson and co-workers and Li and John started using shape memory effect of shape memory alloy wires or SMPs to realize self-healing function of macroscale cracks. Li et al. reported a series of SMP-based self-healing composites and syntactic foams via the close-then-heal strategy. Interestingly, the confined shape recovery functionality was utilized to close the crack and then the melted thermoplastic particles were “sucked” into the crack to realize healing ultimately. Also, strain-hardened SMP fibers were embedded into thermosetting polymer composites, with special structures such
as the grid-stiffened SMP-cored sandwich, 3D woven-fabric-reinforced SMP composites or the sandwich skin, to improve their self-healing property. Mather and co-workers also reported an interpenetrating network (IPN) of cross-linked poly(ε-caprolactone) (n-PCL) and linear poly(ε-caprolactone) (L-PCL).[19–20] The shape recovery of the n-PCL brought the crack surfaces to close proximity, and then the melting and diffusion of the L-PCL healed the crack. It should be noted that the self-healing capability of all these materials was provided by healing agents. Recently, introducing reversible bonds to materials has become another promising approach to construct shape memory assisted SHMs. For example, Wang and co-workers developed a thermally healable shape memory polyurethane containing Diels–Alder (D–A) bonds.[21] The thermoreversible character of D–A bonds endowed the materials with self-healability and the semicrystalline macromonomers served as switching domains rendering the materials shape memory properties. Noncovalent interactions, including hydrogen-bonding,[22,23] metal–ligand binding,[24,25] and host–guest interactions,[26] were also utilized to fabricate self-healable shape memory materials.

Up to now, most shape memory assisted healing behaviors are triggered by heating. However, there is inherent limitation of such materials because direct heating is not safe and realistic for many applications. Therefore, athermal programing processes have been increasingly valued as an appealing new trend. For instance, Zhang and Zhao developed light-triggered shape memory assisted SHMs utilizing the photothermal effect of gold nanoparticles.[27] Using light as a trigger takes the advantage of remote activation, as well as precise control, but it should be noticed that local high temperature is still unavoidable for aforementioned materials. Therefore, very recently, other athermal stimuli, such as redox agent,[26] solvent (ethyl acetate),[28] and metal ion,[25] were explored as candidates to trigger the shape memory assisted healing behavior.

In this study, we prepared novel shape memory assisted SHMs induced by moisture at ambient temperature. Among the stimuli known for SMPs and SHMs, moisture or water has advantages of green, inexpensive, and moderate. To date, materials with either water-induced shape memory property or healing capability have been developed.[29–31] However, it is still challenging to endow both water-enabled functions to a single polymer. The main reason for this difficulty is the conflicting structural requirement of the two types of polymers. SMPs require a permanent network restricting chain motion, while SHMs need high chain mobility. Here, we tried to solve this problem through introducing two kinds of supramolecular interactions into the matrix. We prepared a semi-IPN composed of adamantan (Ad)-grafted poly(methacrylate-co-2-hydroxyethyl methacrylate) (p(HEMA-co-BA)), β-cyclodextrin modified Al2O3 nanoparticles (β-CD-Al2O3 NPs), and polyvinylpyrrolidone (PVP). The hydrogen bonds between hydroxyl groups in p(HEMA-co-BA) and carbonyl groups in PVP functioned as water-sensitive switches, making the materials show moisture-induced shape memory effect. The host–guest interactions (β-CD-Ad) served as both permanent phases and self-healing motifs, enabling the chain mobility at the cracks to increase further and self-healing. In addition, these PVP/p(HEMA-co-BA) semi-IPNs also showed thermosensitive triple-shape memory behavior.

2. Results and Discussion

2.1. Preparation and Characterization of PVP/pHEMA-coBA) Semi-IPNs

The synthetic route of PVP/p(HEMA-co-BA) semi-IPNs is shown in Figure 1a. Al2O3 nanoparticles (NPs) were selected as the filler because they could improve the strength and thermal conductivity of composites. The typical transmission electron microscope (TEM) image (Figure S4a, Supporting Information) shows that the β-CD-Al2O3 NPs have irregular shape with the particle size of 30–45 nm. The X-ray diffraction (XRD) patterns of Al2O3 NPs, NH2-Al2O3 NPs, and β-CD-Al2O3 NPs (Figure S4b, Supporting Information) are very similar, suggesting that the crystalline form of Al2O3 NPs remain unchanged in the functionalization. In the FT-IR spectrum of β-CD-Al2O3 (Figure S4c, Supporting Information), three new characteristic peaks at 1038, 1149, and 1490 cm−1 are observed as compared to the spectrum of Al2O3 NPs, corresponding to νC-O-C, δO-C of β-CD, and δN-H of amide. The νC-C of benzene ring (1369 and 1419 cm−1) disappear as compared to Tos-CD, suggesting that the Al2O3 NPs were modified by β-CD successfully. The weight ratio of grafted β-CD in β-CD-Al2O3 was 18.64% according to the thermogravimetric analysis (Figure S4d, Supporting Information), which corresponds to about 3710 β-CD molecules per Al2O3 NP (calculated according to ref. [32]).

The preparation of PVP/p(HEMA-co-BA) semi-IPNs is through a one-pot copolymerization of PVP, 2-hydroxyethyl methacrylate (HEMA), butyl acrylate (BA) adamantane-modified HEMA (HEMA-Ad), and β-CD-Al2O3 NPs in N,N-dimethylformamide (DMF). Four groups varied in the amount of chemical cross-linking agent were named as sample 1, 2, 3, and 4 (Table 1). The hydroxyl groups (donor) in p(HEMA-co-BA) copolymer systems can form hydrogen bonding with the carbonyl groups (acceptor) on PVP.[33,34] The FT-IR spectra (Figure S5a, Supporting Information) showed that the C=O stretching peak of pure PVP at 1655 cm−1 shifted to 1663 cm−1 when PVP/p(HEMA-co-BA) semi-IPNs formed, indicating the formation of hydrogen bonding. The interaction between Ad and β-CD in the PVP/p(HEMA-co-BA)
semi-IPNs was investigated by 2D infrared spectroscopy (2D-IR) which has been proven to be a powerful tool for studying the molecular interactions in many systems\cite{35,36} (Figure 1b,c, for clarity, not all of the spectra are shown). The characteristic peaks of $\beta$-CD at 1161 and 1082 cm$^{-1}$ and Ad at 1103 cm$^{-1}$ showed obvious correlations, indicating that Ad and $\beta$-CD in the material strongly interacted with each other. Moreover, the morphology of the fracture surface showed that $\beta$-CD-Al$_2$O$_3$ NPs could be distributed uniformly in the matrix (Figure 2a and Figure S5b, Supporting Information). The thermogravimetric analysis (TGA) of the PVP/p(HEMA-co-BA) semi-IPNs (Figure S6, Supporting Information) showed good thermal stability of the materials until the temperature reached up to 250 °C.

Table 1. The components and shape memory properties of PVP/p(HEMA-co-BA) semi-IPNs.

| Sample | HEMA [mL]; BA [mL]; HEMA-Ad [g] | $\beta$-CD-Al$_2$O$_3$ [g] | PVP [g] | EGDMA [µL] | $R_f$ [%] | $R_r$ [%] | $R_f$ [%] | $R_r$ [%] |
|--------|---------------------------------|----------------------------|---------|------------|-----------|-----------|-----------|-----------|
| 1      | 0.5; 2.37; 0.6                   | 0.3                        | 0.66    | 0          | 99.3      | 91.1      | 99.3      | 91.1      |
| 2      | 0.5; 2.37; 0.6                   | 0.3                        | 0.66    | 0.5        | 99.6      | 86.1      | 100       | 95.8      |
| 3      | 0.5; 2.37; 0.6                   | 0.3                        | 0.66    | 1          | 99.3      | 95.5      | 100       | 98        |
| 4      | 0.5; 2.37; 0.6                   | 0.3                        | 0.66    | 2          | 98.9      | 96.9      | 100       | 100       |
| Control 1 | 0.5; 2.37; 0.6                       | 0                         | 0.66    | 1          |           |           | 100       | 100       |
| Control 2 | 0.5; 2.37; 0.6                       | 0.3                        | 0       | 1          |           |           |           |           |
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Hygroscopic tests indicate that the PVP/p(HEMA-co-BA) semi-IPNs have strong water absorption capability. Figure 2b shows that the moisture uptake (wt%) of all the PVP/p(HEMA-co-BA) semi-IPNs are about 27%, suggesting that the influence of cross-link density was little. This good hygroscopicity is the precondition of moisture-induced shape memory effect and self-healing property at room temperature.

Dynamic thermomechanical analysis (DMA) was carried out to obtain the thermal information of PVP/p(HEMA-co-BA) semi-IPNs. As shown in Figure 2c and Table S1 (Supporting Information), the $T_g$ of the samples elevated with the amount of cross-linkers increasing, which is reasonable due to the denser chemical cross-links inhibiting the short-range segment motion. It can also be noticed that there are broad $T_g$ for all the three samples. For example, sample 3 has a broad $T_g$ over 20–140 °C. It may because that the coexistence of the $\beta$-CD-Ad interactions and hydrogen bonding leads to microphase separation and each microphase has different $T_g$.

2.2. Heat-/Moisture-Stimulated Shape-Memory Behavior

The PVP/p(HEMA-co-BA) semi-IPNs showed excellent thermal-induced dual shape memory property (Table 1 and Figure S7, Supporting Information). The shape fixing efficiency ($R_f$) and shape recovery efficiency ($R_r$) could reach to 99.3% and 95.5%, respectively. It is widely accepted that the shape fixity is mainly determined by reversible phases, while the shape recovery primarily lies on the integrity of the permanent phase.[8] In the present work, both host–guest interactions and hydrogen bonding act as reversible phases due to their thermal sensitivity.[37,38] Also, the content of host/guest motifs and hydrogen bonding donors and acceptors were the same in each sample. Thus, the values of $R_f$ reach about 99% for all the samples tested, regardless of the varying cross-linking degrees. On the contrary, it is clear that enhancing the density of permanent network can facilitate the shape recovery process, as the $R_f$ of the samples increased from 86.1% to 96.9% with the increase of cross-linkers.

It was reported that multiple shape memory behavior can be realized when a material had a very broad glass transition region.[39] The PVP/p(HEMA-co-BA) semi-IPNs also exhibit multiple shape memory property due to the broad $T_g$. Figure 3a shows the triple shape memory process of sample 3 recorded through DMA. The original sample (O) was deformed and fixed into two different temporary shapes, A and B, in a shape memory cycle involving three operating temperatures: $T_{high}$, $T_{mid}$, and $T_{low}$, which were set as 90, 50, and 20 °C, respectively. It can be seen for sample 3 that the $R_{f(O\rightarrow A)}$ and $R_{f(A\rightarrow B)}$ are 74.1% and 98.2%, while $R_{r(B\rightarrow A)}$ and $R_{r(A\rightarrow O)}$ are 57.4% and 95.5%. The moduli at different operating temperatures characterized by DMA and their ratio were concluded in Table S1 (Supporting Information). A large difference in moduli (up to 2–3 orders of magnitude for sample 3 in this study) below and above the operating temperatures is the most substantial property to render shape memory function.[40]

For more intuitive illustration, shape manipulations using the Jianzhi technique were given to demonstrate the triple-shape memory effect.[41] As shown in Figure 3b, first, the original circular film with through-line patterns was heated at 90 °C for 5 min, and then deformed into a 3D shape A. This shape can be fixed after cooling to 50 °C, followed by further stretching to a temporary elongated net-shape B which can be fixed by cooling to 20 °C. Reheating the sample to 50 and 90 °C, the shape recovered readily from shape B to shape A first and further to the permanent flat shape. Based on the excellent triple-shape memory property, such complex shape manipulation using the Jianzhi technique may provide appealing potential applications due to the effective of fabricating increasing small structures.

Furthermore, the PVP/p(HEMA-co-BA) semi-IPNs can show moisture-induced shape memory effect at room temperature. The straight specimen of sample 3 was deformed to “C”-like shape through a wetting and drying
process. After being moved to 100% relative humidity (RH) at room temperature for 2 h, it automatically recovered to its original shape with the $R_r$ of 98% (Figure 3c). A large change of moduli in response to moisture (3 orders of magnitude for sample 3 in this study; see Figure S8b in the Supporting Information) was found and caused excellent shape memory effect. This significant decrease of moduli triggered by water is due to the weakening of hydrogen bonding. While the chemical cross-linking points and $\beta$-CD-Ad complexes are stable in water and act as the permanent shape to affect the shape recovery, the hydrogen bonds serve as the reversible phase to determine the shape fixity. To validate this theory, moisture-induced shape memory effect of the sample 1 containing no cross-link agent was also tested. Only slightly declined $R_r$ (91.1%; see Table 1 and Figure S9 in the Supporting Information) was observed, suggesting that the host–guest interactions could act as the fixed phase indeed. In addition, the temporary shape of control 2 with no PVP cannot be fixed, indicating that hydrogen bonding was the key role of reversible phase. A proposed shape memory mechanism is shown in Figure 3d. A number of hydrogen bonds form physical cross-links in the PVP/p(HEMA-co-BA) semi-IPNs. As the moisture diffuses into the polymer network, the materials become soft and can be deformed to temporary shape by external force because the water molecules break the hydrogen bonding. Subsequent drying leads to the reformation of hydrogen-bonded cross-links. As a result, the temporary shape is fixed. In the recovery procedure, moisture absorption in 100% RH leads to broken of hydrogen bonding again, the stored strain is released and the material returns to the original shape driven by the recovery stress arising from the covalently cross-linked networks and host–guest complexes.

Interestingly, the temperature and moisture stimuli are interchangeable. As shown in Figure 3e, a lily-like temporary shape of sample 3 was thermally fixed and recovered in 100% RH at room temperature for 2 h. In a similar way, a starlike shape of the sample 3 was fixed through a wetting and a drying process, and then the temporary shape recovered to original shape at 90°C for 5 min (Figure 3f). It should be noted that the speed of shape recovery is relative slow at room temperature, but heating would help to speed up the shape recovery. For example, it took 30 min to fully recover to the original shape when putting the temporary shape of sample 3 into 100% RH at 50°C (Figure S11, Supporting Information).

2.3. Self-Healing Behavior
It is found that the PVP/p(HEMA-co-BA) semi-IPNs also exhibit self-healing properties. As shown in Figure 4a, the
specimen self-healed after 2 h with small amount of water at room temperature. Images of ultradepth 3D microscope show that a crack with 28.5 μm in width and 0.5 mm in depth almost disappeared after 2 h in 100% RH (Figure 4b). The tensile test was carried out to evaluate the efficiency of self-healing behavior. The results are summarized in Table 2 (also see Figure S12 in the Supporting Information). The self-healing efficiency (η) is calculated by Equation (S10) (Supporting Information). The η of the PVP/p(HEMA-co-BA) semi-IPNs increased with the decline of the cross-linking agents. Sample 1 without covalent cross-links exhibits the highest η (~85%), while sample 4 could only reach a η of 65%. The reason is that the chemical cross-links may limit the conformation change of polymer chains and segmental mobility.

To investigate the self-healing mechanism, we prepared two control samples: control 1 without β-CD-Al2O3 NPs and control 2 without PVP constituent. It was found that control 1 did not exhibit self-healing behavior at all (Figure S13a, Supporting Information) after treating a small amount of water, whereas the self-healing effect of control 2 was observed (Figure S13b, Supporting Information). These results suggest that the host–guest interaction plays the dominant role for healing. To further confirm the key role of the host–guest interactions on self-healing, a drop of β-CD solution was added on the wound of sample 3. Because the free β-CD were able to act as competitive host molecules blocking the formation of inclusion complexes between the guest molecules (Ad) and β-CD moieties in the sample 3,[35,42] it was found that the sample could not realize self-healing (Figure S14, Supporting Information), indicating that the β-CD-Ad interactions are the self-healing motifs of PVP/p(HEMA-co-BA) semi-IPNs. Figure 4b shows the schematic illustration of self-healing of PVP/p(HEMA-co-BA) semi-IPNs. When a PVP/p(HEMA-co-BA) semi-IPN sample was damaged, many supramolecular links were broken near the fracture surface because their strength was lower than that of covalent bonds. After adding water, the mobility of the polymer chains increased because the formation of water–water bridges loosens the

**Table 2.** Mechanical and self-healing properties of PVP/p(HEMA-co-BA) semi-IPNs.

| Sample | $E_T$ [MPa] | $\epsilon$ [%] | $\sigma$ [MPa] | Healing efficiency ($\eta$) [%] |
|--------|-------------|----------------|-------------|-----------------------------|
|        | Original    | After healed   | Original    | After healed   |                  |
| 1      | 0.36        | 337.65         | 0.612       | 0.519           | 85.2            |
| 2      | 7.64        | 173.33         | 0.812       | 0.586           | 72.2            |
| 3      | 9.42        | 161.39         | 1.452       | 0.987           | 68.0            |
| 4      | 15.0        | 98.406         | 2.036       | 1.341           | 65.9            |
hydrogen bonding network in the materials. The diffusion of the polymer chains caused the fracture surfaces close to each other. The nonassociated host and guest groups at the fracture surfaces were “eager” to link together. Therefore, they reformed host–guest complexes across the interface and self-healing happened. However, it should be noted that many covalent bonds were also broken as the sample was damaged. Therefore, the self-healing efficiency was not 100%. This phenomenon has been observed in other supramolecular self-healing polymer systems.\cite{35,42} Additionally, owning to reversibility of host–guest interaction, the PVP/p(HEMA-co-BA) semi-IPNs were able to realize self-healing property more than once, even on the same fracture section (Figure S12, Supporting Information). The drop of the healing efficiency between the second and the first healed sample was possibly due to remnant defects at the site of initial fracture.\cite{4}

It should be noted that the chain diffusion always occurs in microscopic scale. Consequently, damages with large deformation are hard to be self-healed only depend on self-healing procedure. Interestingly, the moisture-sensitive shape-memory behavior of PVP/p(HEMA-co-BA) semi-IPNs could be utilized to assist the self-healing of separated crack. As shown in Figure 5a, sample 3 was damaged and deformed as V-shape. The wound was too wide to be self-healed. As the sample was put into 100% RH environment for 3 h, the film recovered to original shape and the wound on both sides touched each other, and then the crack was healed due to the reformation of \( \beta \)-CD-Ad. Through ultradepth 3D microscope (Figure 5b,c), we can observe that the material crack was almost healed. The mechanism of the whole shape memory assisted self-healing process could be that, as the water loosening the hydrogen bonding network, the stored deformation energy is released and the material returns to the original straight shape. As a result, fracture surfaces gradually come together into needed closure, and then the “broken” host and guest groups at the fracture surfaces reformed host–guest complexes across the interface to repair the materials.

3. Conclusions

In conclusion, we integrated moisture-/thermoinduced shape memory property and self-healing capacity into one material by introducing dual supramolecular interactions into a PVP/p(HEMA-co-BA) semi-IPN. Utilizing both non-covalent interactions (hydrogen bonding and host–guest interaction) as molecule switches, the PVP/p(HEMA-co-BA) semi-IPNs show a broad glass transition and exhibit good thermoinduced triple-shape memory properties. More interestingly, unlike other self-healable shape memory materials, damages with large deformation of PVP/p(HEMA-co-BA) semi-IPNs could be healed by the help of moisture. It is found that host–guest interactions serve as both self-healing motifs and fixed phases, while moisture-sensitive hydrogen bonds switch the chain mobility. This athermal shape memory assisted self-healing ability of our materials shows great values for biomedical and biotechnology applications.

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

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