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Humidity-Responsive Polyvinyl Alcohol/Microcrystalline Cellulose Composites with Shape Memory Features for Hair-Styling Applications

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This study investigates the maintenance of humidity-responsive shape memory polymer composites comprising polyvinyl alcohol (PVA) and cellulose microcrystal for maintaining hair curls in humid environments. The composite films are prepared by a simple blending method using aqueous solutions of different polymer ratios and characterized for thermal properties, chemical structure, and surface morphology. The hydroxyl groups in the PVA and cellulose provided hydrogen-bonding interactions and improved the miscibility of the composites. Increasing the cellulose content in the composites enhanced mechanical properties and curl-shape recovery performance, with 20–25 wt.% cellulose achieving maximum recovery. When the PVA/cellulose solution is applied to natural hair, it effectively maintains the shape of curled hair bundles for at least 6 h under 80% humidity and promotes the hair shape recovery rate to 8–10%. Overall, The proposed humidity-responsive PVA/cellulose composites present promising application potential in the field of hairstyling to withstand humid weather.

1. Introduction

Frizzy hair is a benign problem in the everyday life of modern people. It stems from the penetration of air moisture in the hair cuticle, which results in hair swelling. In particular, in muggy and humid weather, moisture penetrates the hair very actively, leading to a fluffy and frizzy appearance. Modifying the hairstyle using flat ironing to regulate this phenomenon is a very popular method. Nowadays, people prefer to try different hairstyles regularly, instead of adhering to a permanent style. Temporary one-day curls achieved by hot ironing are used on a daily basis, particularly from people with straight hair. In humid environments, however, hair curls are easily compromised; therefore, effective hair curl maintenance products are required to prevent the hairstyle from becoming frizzy and spoiled.

Polyvinyl alcohol (PVA) is a well-known, human skin-compatible, and environment-friendly polymer that is water-soluble, easy to form, non-toxic, and biodegradable.[1,2] To achieve ecological sustainability, PVA has been widely studied for compositing with natural fillers, such as chitosan,[3–5] cellulose,[6–8] and starch.[9–11] Furthermore, PVA composites have been successfully used for drug delivery, contact lenses, filtration materials, and membrane formation.[4,12,13] In addition, the safety assessment of PVA as a binder, thickener, and film-former in cosmetic products, e.g., makeup and skincare, has been verified.[14,15] The hydroxyl

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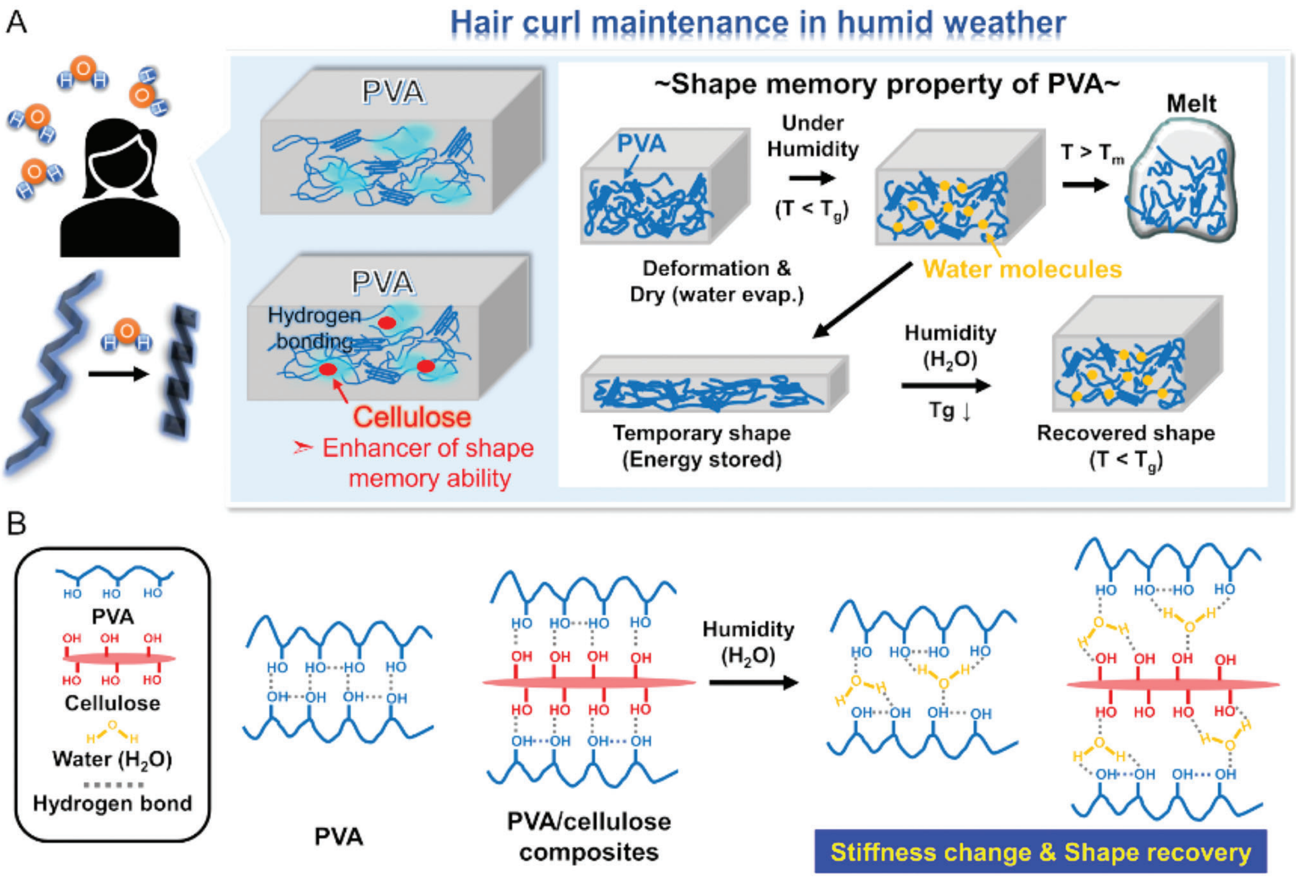

Figure 1. A) Schematic illustration of humidity-responsive shape memory mechanism of PVA/cellulose composites and its application in hair styling. B) Schematic representation of hydrogen bonding interaction among PVA, cellulose, and water molecules.

groups in PVA strongly affect its solubility in water and response to humidity, resulting in water retention and swelling properties. Although these properties provide many benefits to countless users, another attractive property of PVA is its shape memory ability, which has not been fully exploited in the cosmetic products field.

Cellulose is a polysaccharide that constitutes the cell wall of plants and is the most abundant, biodegradable, renewable, and inexpensive polymer found in nature.[16] As such, it has been extensively used in a wide range of fields because of its biocompatibility, hydrophilicity, and thermal stability.[17] Nano- and micro-sized celluloses are employed as well-designed fillers in the medical, cosmetic, filtration, and food packaging fields because their intramolecular hydrogen bonds provide stiffness to the polymer chain and improve the mechanical properties of composite materials.[18–21] The presence of hydroxyl groups in cellulose facilitates the formation of hydrogen bonds with PVA; therefore, good composite properties and satisfactory performance, such as improved mechanical and barrier properties,[22,23] high moisture resistance and thermal stability,[24,25] and superior UV absorption,[26,27] have been achieved through the interaction between cellulose and PVA. Although excellent cellulose-based materials have been successfully applied, more approaches still need to be explored for practical applications.

Despite the existing knowledge on the shape memory performance of PVA, few attempts have been made to improve or enhance its shape memory ability. In fact, the long-term shape memory ability of PVA in humid environments still presents limitations. In this study, we investigate PVA/cellulose composites for application in hair curl maintenance products, with the purpose of improving their shape memory performance in response to humidity (**Figure 1**). The design criteria of our PVA/cellulose composites were to precisely tailor the interaction between PVA and the cellulose filler to enhance the shape memory ability, without compromising the humidity response. Composite films were prepared by mixing PVA and cellulose in different weight ratios (PVA/cellulose = 4/1, 3/1, and 2/1). The thermal properties, chemical structures, and surface morphologies of the PVA/cellulose films were evaluated using differential scanning calorimetry (DSC), Fourier-transform infrared (FTIR) spectroscopy, and scanning electron microscopy (SEM). Furthermore, the moisture absorption and mechanical properties of the PVA/cellulose composite films were evaluated, with the results indicating an excellent shape memory performance even under high humidity conditions. In addition, preliminary findings on hair curl maintenance were obtained by applying a PVA/cellulose solution to a natural hair sample and exposing it to an 80% humidity chamber at ≈30 °C for 6 h. Overall, our proposed PVA/cellulose composite material demonstrates

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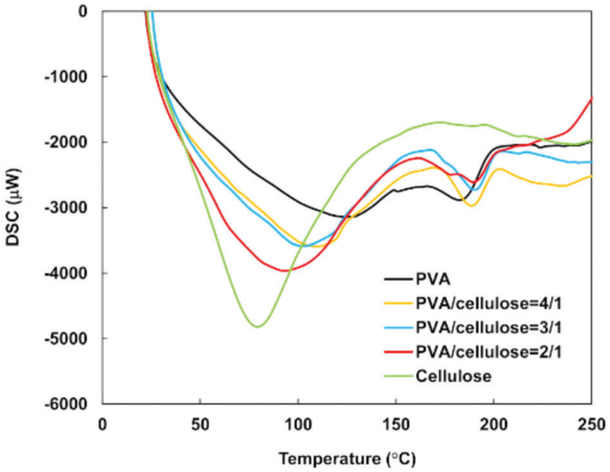

Figure 2. DSC curves of PVA, cellulose, and PVA/cellulose composites with different compositions.

noteworthy potential for a wide range of applications in the cosmetics field.

2. Results and Discussion

2.1. Characterization of PVA/Cellulose Films

2.1.1. Thermal Properties of PVA/Cellulose Composite Films

Homogenization of PVA/cellulose suspensions adjusted to a PVA to cellulose weight ratio of 4/1, 3/1, and 2/1 by stirring and sonication dramatically suppressed the sedimentation of cellulose microcrystals used as filler in all compositions, resulting in uniform composite suspensions (Figure S1, Supporting Information). When films were prepared from the obtained PVA/cellulose suspensions by the solvent casting method, transparent films were obtained with PVA, whereas opaque composite films were obtained with PVA/cellulose (Figure S2, Supporting Information). Regardless of the composition of PVA/cellulose, no macroscopic aggregation of cellulose microcrystals was observed in the composite films, and a relatively uniform film was formed. Thermal characterization is a convenient technique to analyze physicochemical characteristics and changes, such as phase transitions, glass transition temperature (T_g), and melting temperature (T_m). **Figure 2** shows the differential scanning calorimetry (DSC) curves of the as-prepared pure PVA, cellulose, and PVA/cellulose composite films in the temperature range of 25—250 °C at a heating rate of 10 °C min^{-1}. Broad endothermic peaks at ≈80 and 125 °C were observed for the pure cellulose and PVA films, respectively, which were attributed to the evaporation of residual water in the films. The higher evaporation temperature of bulk water in the PVA films, compared to that in their cellulose analogs, suggested that the hydrogen bonds between PVA and water molecules were stronger than those between cellulose and water molecules. Ergo, the water evaporation temperature of the PVA/cellulose composite films strongly depended on their composition, shifting toward lower temperatures (from 110 to 93 °C) as the cellulose content increased.

PVA forms crystals through inter- and intramolecular hydrogen bonding and, as expected, shows another endothermic peak on the higher temperature range, with a T_m of 182 °C. Interestingly, the compositing of PVA with cellulose, which does not exhibit a T_m, resulted in an increase of the T_m of PVA to ≈190 °C. PVA-polyethylene glycol (PEG) composite materials, using PEG instead of cellulose, are known to possess lower T_m values owing to PEG addition.[28] In this case, it was inferred that the hydrogen bonds formed between PVA and PEG disrupted the regular structure and movement of the PVA chains, resulting in a lower T_m for PVA. Conversely, the PVA/cellulose composite films in this study exhibited an increased T_m by ≈8 °C regardless of composition, suggesting that the hydrogen bonds formed between PVA and cellulose enhanced the regular structure and mobility of the PVA chains.

The evaporation temperature of the PVA/cellulose composite films was observed as a single peak, regardless of the PVA composition, similar to the T_g observed in the PVA/cellulose system.[29,30] Furthermore, rather than demonstrating a simple decrease in enthalpy, the T_m of PVA shifted to a higher range owing to its compositing with cellulose. These results suggest that the composites formed a miscible homogeneous phase, highlighting the capability of cellulose as a filler to establish strong hydrogen bonds with PVA during film formation. As discussed below, the compositing of PVA with cellulose has a marked effect on its hydrogen bonding performance by altering its crystallinity, in turn enhancing its mechanical properties and humidity response.

2.1.2. Chemical Structure and Intermolecular Interactions of PVA/Cellulose Composite Films

The as-prepared PVA/cellulose composite films were then characterized using Fourier-transform infrared (FTIR) spectroscopy to identify their chemical structure and interaction between PVA and cellulose (**Figure 3**). The FTIR spectra of the pure PVA film showed characteristic peaks at 3302, 2943, 1419, and 1087 cm^{-1}, assigned to the O–H stretching, C–H stretching, C–H bending, and –C–O– stretching vibrations, respectively.[6,31] Another characteristic peak was observed at 1735 cm^{-1}, attributed to the C=O stretching vibration, which originated from the unhydrolyzed acetate group on PVA. The FTIR spectra of the PVA/cellulose composite films exhibited additional absorption bands at 1159 and 1051 cm^{-1}, corresponding to C–O–C glycosidic ring stretching, C–O/C–C asymmetric stretching, and O-C-H bending vibrations of cellulose, respectively, suggesting the presence of cellulose in the composite films.[32,33] On the other hand, both the pure PVA and PVA/cellulose films exhibited a wide O–H stretching vibration band in the range of 3000–3700 cm^{-1}. Within this region, the O–H stretching vibration bands corresponding to the free alcohols in the amorphous phase and the bound alcohols in the crystalline phase appeared at 3600–3650 and 3200–3570 cm^{-1}, respectively.[28] The band at 3302 cm^{-1} in the PVA film, originating from the bonded hydroxyl groups in the crystalline phase, shifted to a lower wavenumber upon compositing with cellulose, and the level of the shift became larger as the cellulose content increased (3286, 3287, and 3283 cm^{-1} at PVA/cellulose ratios of 4/1, 3/1, and 2/1, respectively). PVA

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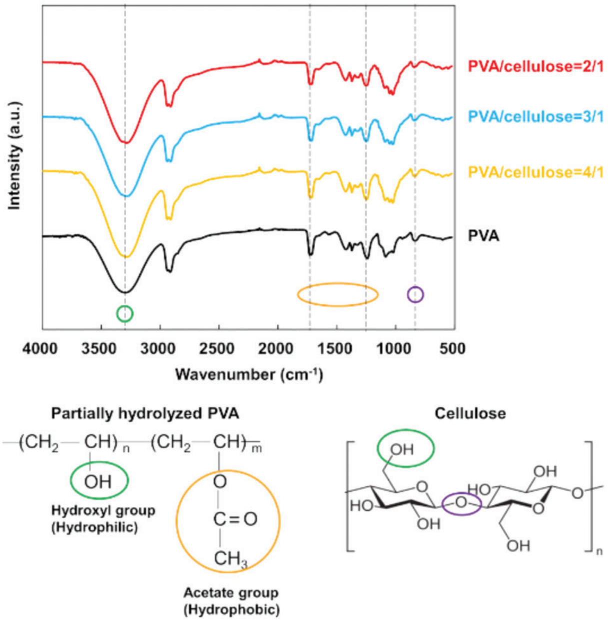

Figure 3. FTIR spectra of PVA and PVA/cellulose composite films with different compositions. The figure below shows the chemical formulas of PVA and cellulose used in this study, with the functional groups circled in colors corresponding to the FTIR spectral assignments.

forms intra- and intermolecular hydrogen bonds via side-chain hydroxyl groups, while PVA/cellulose composite films can form additional hydrogen bonds between PVA chains and cellulose. The shift of the bonded hydroxyl groups in the crystalline phase of PVA toward a lower wavenumber indicated that the newly formed hydrogen bonds between PVA and cellulose were more robust than those in pure PVA, which was consistent with the DSC results showing that the T_m of PVA was improved by compositing with cellulose. Therefore, it was inferred that the presence of cellulose in the PVA matrix acted as a filler that enhanced hydrogen bonding in the PVA/cellulose composite films.

2.1.3. Surface Morphology

In addition to the appearance of the films, the DSC and FTIR results above indicate that when cellulose is used as a filler in PVA/cellulose composite films, it is homogeneously dispersed and forms hydrogen bonds that affect the thermal properties of the film. To investigate the compatibility of the PVA and cellulose components within the film structure, the surface morphologies of the resultant films were observed using scanning electron microscopy (SEM) (**Figure 4**). The cellulose used as filler in this study had a plate-like microcrystal morphology with a long axis length of 10–70 µm, and its cast film surface was uneven and rugged. On the other hand, the PVA/cellulose composite films exhibited a more homogeneous and smooth surface morphology, although unevenness derived from the cellulose microcrystals could still be observed. As the PVA content of the composites increased, the surface structure became smoother. Cellulose microcrystals comprise strong intra- and intermolecular hydrogen bonds and are simultaneously insoluble and highly dispersible in water, because of the hydroxyl groups present on their surface. In PVA/cellulose composites, interfacial interactions such as hydrogen bonding between the PVA chains and cellulose microcrystals largely improve the dispersibility and miscibility of cellulose in PVA matrices, resulting in a more uniform and homogeneous surface morphology.[34] The homogeneity and dispersibility of cellulose microcrystals in the composites strongly depend on the PVA content, with higher PVA ratios having a more positive effect on physical homogeneity. Overall, the results of controlling the interfacial interactions between the matrix components and the cellulose used as a filler to enhance dispersion in the composite were consistent with previously reported results.[35]

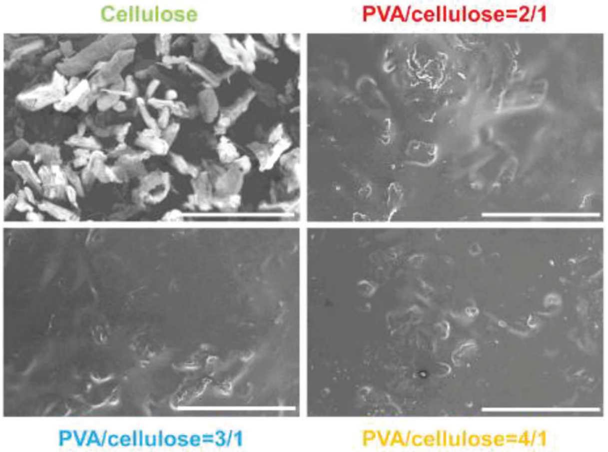

Figure 4. SEM images of cellulose microcrystals and PVA/cellulose composite films with different compositions (scale bar = 100 µm).

2.2. Humidity-Responsive Properties of PVA/Cellulose Composites: Moisture Absorption and Mechanical Properties

PVA owes its high water absorption properties to the presence of hydroxyl groups; however, swelling and dissolution in water can severely hinder the performance of PVA as a hair-coating agent. Compositing PVA with hydrophobic fillers and other materials has been widely considered to enhance its water resistance.[36,37] Since the moisture absorption behavior under high humidity and its equilibrium state are essential for evaluating the performance of PVA/cellulose composites, we comparatively investigated the moisture absorption behavior of pure PVA and PVA/cellulose composite films under 100% relative humidity conditions by tracking the changes in the film weight (**Figure 5**A). Both the pure PVA and PVA/cellulose composite films showed an increase in weight owing to moisture absorption and swelling when exposed to 100% humidity. Specifically, a relatively fast increase in the swelling rates was observed during the initial 3 h, with recorded values of 1.41 for the PVA films and 1.24-1.32 for the PVA/cellulose composite films, indicating that the addition of cellulose reduced moisture absorption. The reason for the increased initial swelling rate in the PVA/cellulose composite films, especially with a PVA/cellulose ratio of 4/1, was the increase in the surface area of the composites, as observed by SEM, or the hydrogen bonding of water molecules to the free

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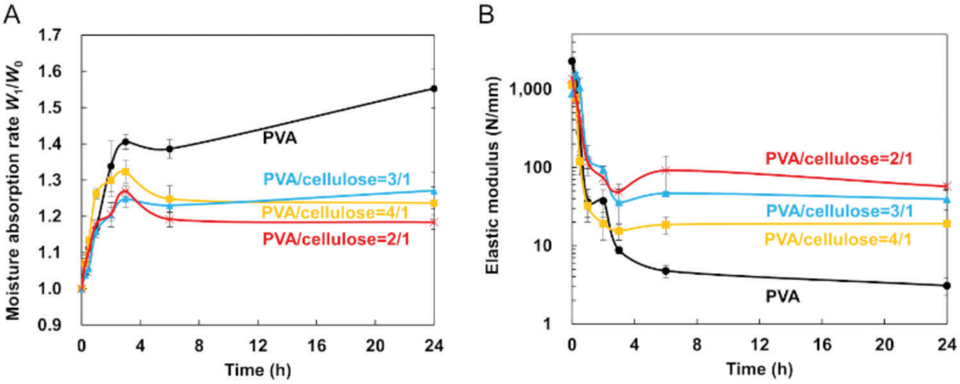

Figure 5. Time course of A) moisture absorption and B) mechanical property changes of PVA and PVA/cellulose composite films with different compositions under 100% relative humidity exposure.

hydroxyl groups of cellulose, which promoted the diffusion of water molecules to the cellulose microcrystal interface.[32] Interestingly, the swelling of the film showed a small peak after 3 h, and the swelling rate tended to decrease slightly after 6 h. Similar reductions in the swelling rate upon moisture or water absorption have been reported for other PVA-based materials.[38,39] On the other hand, pure PVA absorbed more water, with its moisture absorption rate reaching 1.55 after 24 h, in contrast to the saturated moisture absorption changes of the PVA/cellulose composites. In the pure PVA films, moisture absorption was driven by the hydroxyl groups of PVA attracting water molecules through hydrogen bonds, until reaching 100% equilibrium at 100% humidity. On the other hand, the strong intra- and intermolecular hydrogen bonds in the composite films blocked water molecules from accessing the cellulose microcrystal interiors. Thus, increasing the cellulose content in the composite films decreased the volume fraction of the PVA matrix, which contributed positively to the swelling and moisture absorption and resulted in a composition-dependent saturated-type moisture absorption behavior.

The wetting behavior of water on the surface of PVA/cellulose composites was evaluated by contact angle measurement (Figure S3, Supporting Information). The contact angle of the dry PVA film immediately after the drop of water was 91.5 ± 9.6°. Compositing PVA with cellulose microcrystals affected the wettability of the films, with contact angles of 85.0 ± 12.3, 77.5 ± 4.3, and 108.2 ± 10.1° for films with PVA to cellulose ratios of 4/1, 3/1, and 2/1, respectively (Figure S3B, Supporting Information). The cellulose content of the composite film at 25 wt.% was found to be predominantly hydrophilic, while further increase in cellulose content was found to be hydrophobic. Changes in surface chemical structure with time occur on film surfaces in contact with water, resulting in the contact angle values after 300 s were 83.0 ± 7.8, 76.5 ± 13.7, 63.2 ± 4.7, and 82.8 ± 4.2° for PVA and PVA/cellulose composite films with 4/1, 3/1, and 2/1 ratios, respectively. Interestingly, while a wetting ridge was observed in the PVA film a short time after the drop of water, no such ridge was observed in the PVA/cellulose composite film in either composition (Figure S3A, Supporting Information). The formation of a wetting ridge may indicate that PVA swells in contact with water rather than dissolves,[40,41] suggesting that this swelling behavior is significantly suppressed by compositing PVA with cellulose. These results suggested that the moisture absorption rate of the PVA/cellulose composites can be effectively controlled by the cellulose content.

The water or moisture absorption in PVA and its composite films significantly affects their mechanical properties, which in turn plays an important role in understanding the internal structure of a material. Figure 5B shows the change in the elastic modulus of films exposed to 100% relative humidity for a given time. Here, both the PVA and PVA/cellulose composite films showed a rapid decrease in their elastic modulus after moisture absorption for 3 h. The decrease in the modulus due to moisture absorption was significantly suppressed by the presence of cellulose, and the moduli of the PVA/cellulose composites after 24 h were 6 to 18 times higher than that of the PVA film. The degree to which the elastic modulus reached equilibrium after moisture absorption was strongly correlated with the cellulose content in the composites, clearly indicating that the presence of cellulose resulted in the structural strengthening of the film under wet conditions. In other studies on PVA/cellulose composites, it has been shown that the mechanical properties, such as the elastic modulus and tensile strength, were improved several-fold when 20% to 90% cellulose was introduced, without considering moisture absorption.[42–44] In this study, the effect of the cellulose filler on the films' mechanical properties was more pronounced under wet conditions. The presence of free hydroxyl groups in PVA attracted water molecules, resulting in the disruption of hydrogen bonds in the PVA matrix, which in turn reduced the mechanical properties. Thus, water molecules acted as plasticizers in this system. As shown by the moisture absorption properties in Figure 5A, the PVA/cellulose composites exhibited reduced moisture absorption and film swelling rates depending on the cellulose content. Because the films were fully plasticized at the equilibrium swelling state after 24 h, the elastic modulus of the composite films was considered to be dictated by the crosslink density. The DSC and FTIR results in Figures 2 and 3 further corroborate the formation of additional strong hydrogen bonds between the PVA chains and cellulose fillers. In the PVA/cellulose composites, hydrogen bonds existed as cross-linking points that remained stable under wet conditions. In other words, the interfacial interactions, primarily hydrogen bonds, between the PVA chains and cellulose fillers remained undisturbed and stable when exposed to wet environments. These results suggested that

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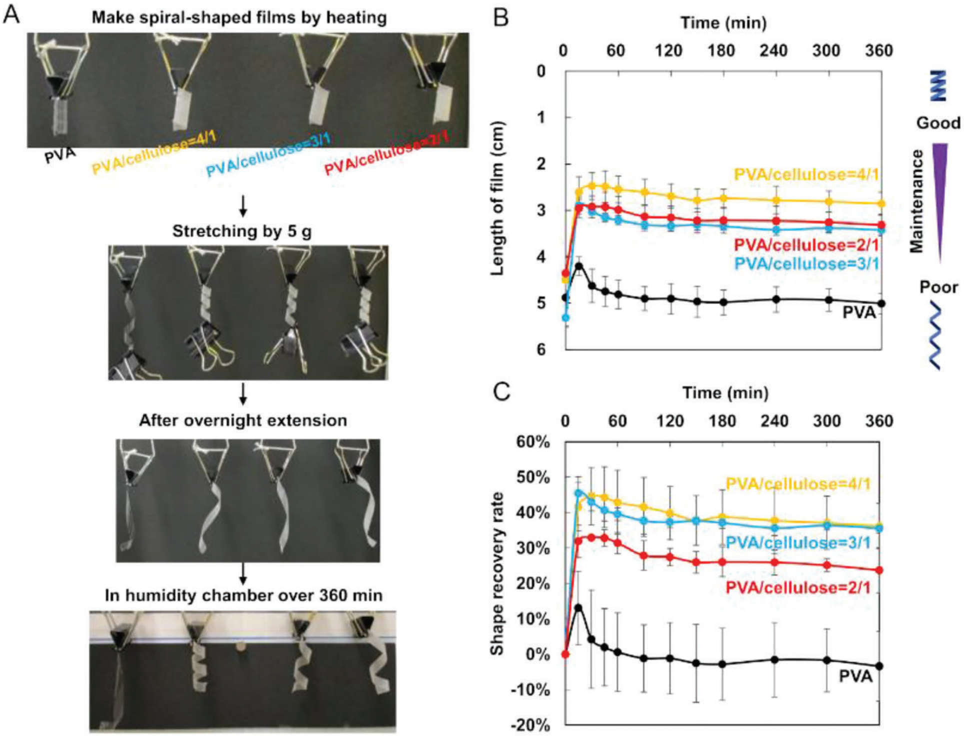

Figure 6. A) Photographs of humidity-responsive shape fixation and shape recovery process for spiral-shaped PVA and PVA/cellulose composite films. Time curves of B) long-axis length and C) shape recovery rate of temporarily stretched spiral-shaped films under exposure to 100% relative humidity.

our PVA/cellulose composite films can greatly mitigate the loss of mechanical properties associated with moisture absorption and swelling, and can thus be employed in a variety of applications.[45]

2.3. Humidity-Responsive Shape Memory Performance of PVA/Cellulose Composites: Shape Maintenance and Recovery Ability

Typical PVA hydrogels form many hydrogen bonds between their molecular chains and have the potential to become shape memory materials driven by the reversibility of hydrogen bonds and the decrease in the glass transition temperature in response to moisture absorption.[46,47] However, pure PVA cannot sufficiently function as a shape memory material in a wet environment, unless chemical cross-linking is introduced.[48,49] Recently, it was reported that the shape memory capacity of PVA can be improved by introducing additional intermolecular hydrogen bonds via compositing with specific compounds that promote hydrogen bonding.[50–52] Therefore, the humidity-responsive shape memory behavior of PVA and PVA/cellulose composites was investigated.

As shown in **Figure 6**, the PVA/cellulose films exhibited clear shape fixation and shape-recovery abilities even after moisture absorption. Films with a permanent spiral shape were prepared by heating a sample placed in an indoor humid environment at 120 °C for 30 min while it was being deformed (Figure 6A). The heat treatment of the PVA and PVA/cellulose films at 120 °C allowed the creation of a new permanent shape with the removal of residual water and the reformation of hydrogen bonds in the films, and the resulting films showed a clear T_g ≈70 °C, independent of their composition (Figure S4A, Supporting Information). The spiral-shaped film was allowed to stand overnight while a 5 g load was applied, and then changed to a stretched shape (temporary shape) when the load was removed. The change from a spiral shape to a temporarily extended shape was attributed to the elongation of the PVA chains owing to the breakage of the relatively weak hydrogen bonds under a force load, that prevented the elongated chains from maintaining their expanded shape.[53] This force-induced stretching of the spiral shape (Figure 6B shows the length of film at 0 min) was slightly suppressed in the PVA/cellulose composites, compared to pure PVA. On the other hand, when the temporarily-extended spiral-shaped films were exposed to high humidity, a decrease in length was observed in all samples in the first 15 min, implying a shape recovery to the original spiral shape (Figure 6B). Figure 6C shows the degree of shape recovery relative to the original spiral shape. After 15 min of exposure to high humidity conditions, the shape recovery rates were 42%, 45%, 31%, and 13% for PVA/cellulose ratios of 4/1, 3/1, and 2/1 and pure PVA, respectively. This clearly shows that the PVA/cellulose composites exhibited superior shape recovery compared to the pure PVA films, in addition to a higher resistance to deformation under force loading. Although the pure PVA film showed a slight shape recovery after 15 min, it also lost its original spiral shape after prolonged exposure to a high-humidity environment. In contrast, the PVA/cellulose composites were able to maintain their spiral shape after recovery for a longer period, with a shape recovery rate of 36%, 36%, and 24%

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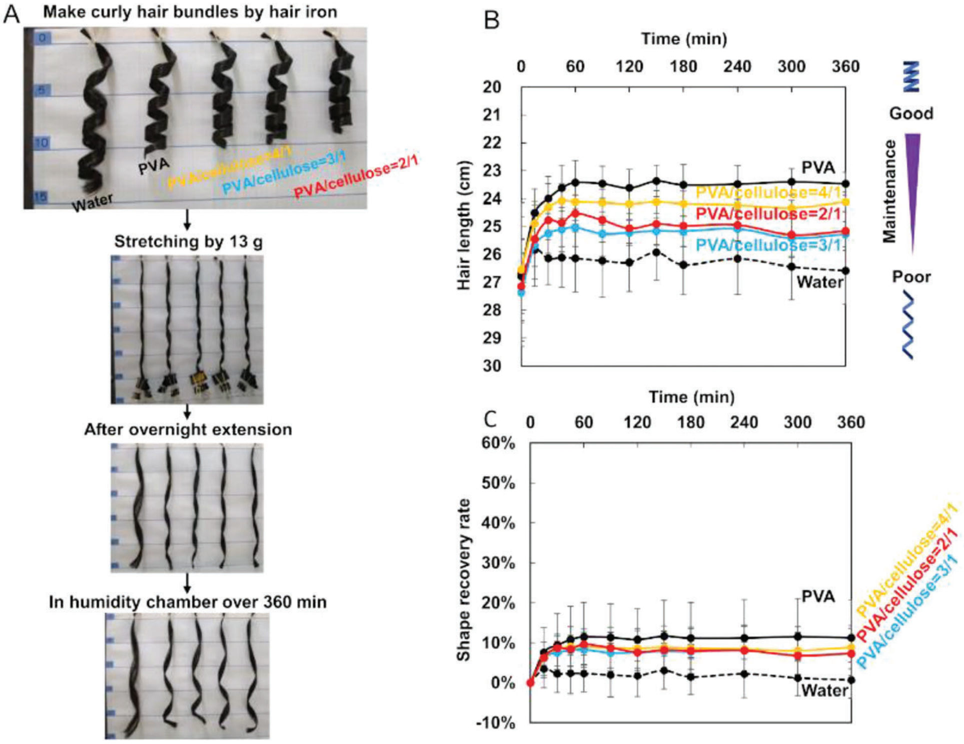

Figure 7. A) Photographs of humidity-responsive shape fixation and shape recovery process of curly hair bundles coated with PVA and PVA/cellulose composites. Time curves of B) length and C) shape recovery rate of temporarily stretched curly hair bundles when exposed to 80% relative humidity.

for PVA/cellulose ratios of 4/1, 3/1, and 2/1, respectively, after 360 min. The main driving force behind the shape recovery was the glass/rubber transition associated with moisture absorption, where water molecules disrupted the hydrogen bonds in the film and simultaneously acted as plasticizers, shifting the T_g of the PVA matrix toward a lower value.[46] Under ambient humidity, the T_g of PVA and PVA/cellulose composites (≈70 °C in dry condition) was higher than room temperature (25.5 ± 1.5 °C), allowing them to maintain their temporary shape; however, under high humidity conditions, the T_g decreased below the room temperature, causing gravity-defying shape recovery owing to entropy elasticity.

These results also indicated that the hydrogen bonds formed between the PVA chains and cellulose provided sufficient and stable cross-linking points to maintain the original spiral shape, even after prolonged exposure to high-humidity conditions. Interestingly, in the 20%–33% cellulose content range, there was no linear correlation between the cellulose content in the PVA/cellulose composites and the shape recovery ability. Although the PVA chains initially contributed to shape fixation and recovery significantly, upon moisture absorption for 1 h, the shape-recovery rate dropped to almost 0% because of the collapsing hydrogen bonds and the subsequent impairment of the mechanical properties. The PVA composite with the highest cellulose content of 33% exhibited lower moisture absorption and higher mechanical strength (Figure 5); however, its shape recovery was inferior to those with ratios of 20% and 25%. These results indicated that the quantitative balance between the PVA matrix responsible for shape memory switching, and the cellulose microcrystals providing stronger hydrogen bonds, is critical for achieving optimal shape memory properties. Here, the maximum shape recovery and retention rate of the recovered shape was achieved at a cellulose content of 20%–25% (PVA/cellulose composition of 4/1 to 3/1).

2.4. Application of PVA and PVA/Cellulose Composites on Natural Hair

Animal hair, including human hair, is composed of α-keratin fibers, a water-sensitive shape memory polymer, that exhibits shape-fixing and shape-recovery properties owing to the recombination of intra- and intermolecular hydrogen bonds in the keratin molecules.[54,55] However, its ability to maintain fixed hair shapes in humid environments is low, creating a need for new products that can effectively maintain hairstyles.

To investigate whether PVA and PVA/cellulose composites can be used to maintain hairstyles under high humidity conditions, aqueous solutions with different PVA/cellulose ratios were applied directly to natural hair, and curls were created using a hair iron at 180 °C. Experiments with films confirmed that heat treatment at 180 °C, the ironing temperature, has little effect on the T_g of PVA and PVA/cellulose composites (Figure S4B, Supporting Information). As a control sample, non-polymer-containing water was used to create a curl shape in the same way (**Figure 7**). Although all curly hair bundles were adjusted to the same length during hot ironing, the water-treated bundles were longer than their PVA- and PVA/cellulose composite-treated equivalents (Figure 7A). This indicated that the inherent shape memory properties of hair can be greatly improved by coating

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with polymer composites. The length of hair swatches when PVA-coated hair was curled on the hair iron was L_{curl}, and the actual length of hair swatches after ironing at 180 °C for 30 s and then removing from the hair iron is L. The shape fixing rate (R_{f}) of PVA-coated hair can be calculated by R_{f} (hair) = L / L_{curl} x 100, and the shape fixing rate of hair bundle $R_{\mathrm{f\,(hair)}}$ value was 93.7 ± 3.6%. The hair samples coated with PVA were found to stretch 31.3 ± 1.9% under their own weight when hung for evaluation (e.g., top photo in Figure 7A). When the curled hair bundles were then stretched overnight by applying a force load, as in the film shape memory test (Figure 6), there was no significant difference in their lengths; however, compared to water, the PVA and PVA/cellulose coatings notably suppressed spreading and frizzing. When the temporarily stretched hair bundles were placed in a chamber with 80% relative humidity, their lengths were shortened by returning to the original curly hair shape. After 360 min of high-humidity exposure, the water-treated hair bundle showed the poorest curl retention, while the hair bundles coated with PVA and the composite solution with a PVA/cellulose ratio of 4/1 maintained their curl shape better than the other compositions (Figure 7B). As shown in Figure 6, the PVA/cellulose composite films showed a significantly higher shape recovery rate and subsequent shape maintenance than pure PVA, and the PVA film did not show any notable shape recovery performance after exposure to high humidity for an extended period, whereas the PVA and composite-treated hair bundle recovered ≈10% of its shape and maintain it thereafter.

Hydrogen bonding between the hair and the applied material is crucial for hair styling. Here, although the application of PVA or the PVA/cellulose composite had a strong enhancing effect on the shape memory of the hair curls, no significant shape recovery was observed when applying the film. The interaction between hair and the coating material is paramount for realizing a shape memory action. Because the PVA and cellulose used in this study are hydrophilic and neutral, their interaction with hair was considered to primarily stem from hydrogen bonds. Under insufficient hydrogen bonding between the hair and the coating, the force generated by the shape-recovery effect of the applied material cannot be transferred to the hair. Furthermore, it is possible that the cellulose microcrystals used in this study were relatively large in size, and thus inefficiently incorporated into the PVA matrix formed on the hair; in fact, in PVA-coated hair bundles, the formation of PVA film was observed between hairs by digital microscopy (Figure S5C, Supporting Information), but it was clearly thinner than the size of cellulose microcrystals, and this could have led to the poor performance observed when the PVA/cellulose composite film was directly applied on hair. Nevertheless, the presence of the coating effectively inhibited water penetration into the hair under high humidity, resulting in reduced hair bundle spreading and frizz formation. Furthermore, the PVA coated on the hair could be easily washed off with warm water or shampoo, despite its stability under high humidity conditions (Figure S5, Supporting Information). As such, our preliminary findings showed that our proposed PVA/cellulose composite coating can slightly restore and maintain the curly shape of stylized hair under heavy-humidity conditions. In the future, it will be important to develop hair-coating agents with ionic and hydrophobic properties that can effectively improve interaction with the hair even with thin application.

3. Conclusion

The chemical structure, thermal and mechanical properties, surface morphology, and shape memory retention of PVA/cellulose composite films with different compositions in response to humidity were investigated. The PVA/cellulose composites showed good compatibility and miscibility owing to efficient hydrogen bonding, allowing the formation of uniform films. The presence of hydrogen bonds formed between PVA and cellulose in the composite, as revealed by chemical structure analysis, affected the film's thermal, hygroscopic, and humidity-responsive shape memory properties. When PVA films are exposed to high humidity conditions, moisture absorption persists for a long period of time until equilibrium is reached, resulting in a decrease in mechanical strength. The compositing of PVA with cellulose markedly inhibits the uptake of water molecules into the film and allows the film to maintain low moisture absorption states for long periods of time. PVA/cellulose composites can also maintain high mechanical properties during moisture absorption, and a positive correlation was observed between the composition of the composite and its mechanical properties. Evaluation of humidity-responsive shape memory using films showed that composites with cellulose content from 20% to 25% exhibited superior shape recovery and maintenance, whereas those with cellulose content of 33% adversely reduced their performance. These results suggest that cellulose is an effective filler to reinforce PVA against humidity, and that the balance between PVA and cellulose content in the composite is critical to achieve both moderate moisture absorption (water) resistance and shape memory properties. Preliminary experiments with natural hair samples showed that both pure PVA and PVA/cellulose composite films can effectively maintain the hairstyle under high humidity conditions, while preventing spreading and frizzing. Particularly, when exposed to 80% relative humidity, natural hair coated with PVA or PVA/cellulose composites showed an ≈10% shape recovery rate from a temporarily extended state to the original curly shape. To the best of our knowledge, this is the first study to report the application of PVA and PVA/cellulose composites as humidity-responsive shape memory polymer hair coatings that help style maintenance via moisture-absorption prevention. When directly applied to hair, the effect of compositing PVA with cellulose was barely noticeable; however, the composite film showed promising results under experimental conditions. For future practical applications of PVA/cellulose composites as moisture-resistant coatings or styling agents on hair, further research will be needed to increase the affinity and interaction between the hair and the polymers and fillers.

4. Experimental Section

Materials: PVA (degree of polymerization 1700, saponified 88%), microcrystal cellulose, and Japanese hair swatches were obtained from NIHON L'ORÉAL K.K (Tokyo, Japan). All other chemicals used in this study were of laboratory grade.

Preparation of PVA/Cellulose Polymer Solutions and Films: 10 wt.% PVA aqueous solution was prepared using 20 g PVA and 180 g distilled water in a glass bottle. After stirring for 30 min at room temperature (in this study, the range of 24—27 °C), the glass bottle was continuously stirred at

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95 °C in an oil bath with a half-sealed cap for 3 h. The PVA aqueous solution was then cooled down to room temperature and stirred until producing a homogeneous solution. For the PVA/cellulose blend solution, an aqueous solution with 10 wt.% cellulose suspension was prepared first, and then mixed with a 10 wt.% PVA solution at PVA/cellulose weight ratios of 2/1, 3/1, and 4/1. For example, for PVA/cellulose = 2/1, 8 g of 10 wt.% PVA solution was mixed with 4 g of 10 wt.% cellulose solution. After homogenization via stirring for 1 h and ultrasonication, 10 g 10 wt.% of the blend solution was added to the cast film. Air bubbles were removed from the blended solution through sonication for at least 30 min. The films were cast by pouring 8 g of each blend solution with different PVA/cellulose ratios into a plastic dish with a diameter of 10 cm. The dishes were incubated overnight on a horizontal stand in a 60 °C oven. Finally, the PVA/cellulose films were peeled off from the dishes using tweezers after cooling to room temperature. The PVA/cellulose films were half-transparent with a thickness of ≈0.13 mm.

Characterization of PVA/Cellulose Films: The thermal properties of the films (5 mg) were evaluated using differential scanning calorimetry (DSC, EXSTAR6000, Seiko Instruments Inc., Japan) at a heating rate of 10 °C min^{-1}. Attenuated total reflection-Fourier transform infrared spectroscopy (ATR-FTIR) measurements were performed for film surface analysis using a Thermo Scientific Nicolet 4700 spectrometer (Thermo Scientific, Waltham, MA, USA). The morphology of the films was observed using scanning electron microscopy (SEM, S-4800, Hitachi High-Technology, Tokyo, Japan). The films were coated with a 30 s gold sputter before observation. The contact angle values for PVA and PVA/cellulose composite films were measured using a contact angle meter (Drop Master-SA-Cs 1, Kyowa Interface Science Co., Ltd., Japan). Water was used as the probe liquid, and images of the contact angle were taken every 100 ms for 300 s after 5 µL water was dropped on the film surfaces. The results are reported as the mean ± standard deviation, $n > 5$.

Moisture Absorption and Mechanical Properties of PVA/Cellulose Films: The films were cut into 0.5 × 3 cm dimensions and dried at 100 °C overnight to remove all the absorbed water. Then, they were placed in a chamber with 100% humidity. The films were removed after 15, 30 min, 1, 2, 3, 6, and 24 h, respectively. The moisture absorption was calculated as the ratio of the film weight after absorption (W_1) to that before absorption (W_0). The elastic moduli of the films were determined using a tensile test machine (EZ-S, Shimadzu Co., Japan). The results are reported as the mean ± standard deviation, $n = 3$.

Shape Memory Properties of PVA/Cellulose Films and Hair Swatches: The shape memory evaluation included three main steps: 1) curl shape making, 2) stretching the curls, 3) humidity-responsive curl recovery. The films were cut into 0.5 × 6 cm pieces and enwound on a glass stick, on which they were fixed by clipping. The glass stick was incubated in an oven at 120 °C for 30 min to produce a spiral-shaped film. The films were then removed from the glass stick after cooling to room temperature. A 5-gram load was then applied to the spiral-shaped films, left overnight at indoor humidity, and then the load was removed to produce temporarily extended spiral-shaped films. The films were then placed in a chamber with 100% relative humidity at room temperature to evaluate their humidity-responsive shape memory performance. This process was video recorded for 6 h to produce a time-lapse movie, from which the length of the films was analyzed using the ImageJ software (National Institutes of Health, Bethesda, MD). The shape memory properties were evaluated through the film length before and after the humidity treatment. The shape recovery rate was calculated as $(L_0 - L_{\min})/L_0$ (L_0 = film length after overnight extension; $L_{\min}$ = film length in a specific minute in the humidity chamber).

For preliminary application in hair styling, Japanese hair swatches (1 g) were coated with 300 µL of 3 wt.% PVA/cellulose solutions (2/1, 3/1, 4/1), pure PVA, and water. After forming curls via hair ironing at 180 °C for 30 s, the curly hair bundles were extended using 13 g weights via the same method described above. The hair swatches were then put under 80% humidity at ≈30 °C for 6 h to record a time-lapse movie. The hair curl maintenance and shape recovery rate were analyzed in the same way as with the films. The results are reported as the mean ± standard deviation, $n = 3$. The surface morphology of clean hair, PVA-coated hair, and PVA-coated hair that had been washed with warm water or shampoo was obtained by digital microscopy. Images of pristine hair, PVA-coated curly hair before and after warm (42 °C) water or shampoo washing were acquired by the bright field mode of digital microscopy.

Supporting Information

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

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Conflict of Interest

The authors declare no conflict of interest.

Data Availability Statement

The data that support the findings of this study are available from the corresponding author upon reasonable request.

Keywords

hair curl maintenance, humidity response, polyvinyl alcohol/cellulose composite, shape memory composite

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