Enhancing the penetration of ingredients into hair fibers using carbonated water

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Abstract

Background: Low penetration performance is a major issue for ingredients that affect hair internally. Therefore, the penetration of ingredients must be enhanced. For example, although aromatic sulfonates can loosen the hair curls without damage, this treatment requires considerable time to achieve tangible effects. Herein, we have developed a novel method to enhance the penetration of ingredients into the hair. Especially, we studied the possibility of enhancing the penetration using carbonated water, which promotes hair swelling.

Methods: A *p*-toluene sulfonate (PTS)-containing formulation was carbonated by introducing carbon dioxide. The hair curl radius and the hairstyle were compared before and after the treatment. Furthermore, the change in the internal structure of the hair was analyzed.

Results: The carbonated PTS solution could reduce the curl-loosening time to 1/4, and regular hair wash using the carbonated PTS-containing shampoo improved the hairstyle. Contrary to expectations, the carbonated water did not change the total penetration amount of PTS. However, carbonic acid could facilitate the penetration of PTS into the macrofibrils based on its ability to make the macrofibrils flexible. We believe that this function results in the sufficient reach of PTS into the structure within the macrofibrils and enhances the curl-loosening effect.

Conclusion: We have successfully developed a technology for promoting the penetration of aromatic sulfonates into the hair using carbonated water. The carbonated PTS-containing shampoo can introduce the concept of stress-free styling with hair washing and may transform the world of rinse-off products. Moreover, carbonated water can potentially enhance the penetration of various functional ingredients.

Keywords: penetration enhancement; carbonated water; curl loosening; rinse-off product; *p*-toluene sulfonate

1. Introduction

Hair care problems for consumers have been insufficiently resolved in various fields such as hairstyles, hair colors, smoothness, and softness. Therefore, we have been developing hair care technology using ingredients that can overcome these problems. However, when hair care ingredients affect the structure within the hair fiber, low penetration performance results in an unsatisfactory effect of the hair care product, which is a major issue encountered when applying such hair care ingredients. Therefore, it is necessary to control the penetration of the hair care ingredients.

A major hair care problem is the difficulty in styling curly hair. Therefore, to manage this hair care problem, many consumers use styling products containing ingredients such as polymers and oils. However, a long styling time is required to obtain a sufficient effect. Furthermore, the styling effect does not last long because it is washed away in the next hair wash. Although several consumers opt for the chemical hair-straightening method for relaxing the hair, it may lead to permanent hair damage.

In previous studies, we reported a technology that can loosen the hair curls without damage by immersing the curly hair fibers in an aromatic sulfonate solution [1,2]. However, this treatment requires considerable time to achieve tangible effects because the aromatic sulfonate affects the macrofibrils in the hair cortex. The aromatic sulfonate is required to pass through the endocuticle and/or cell membrane complex (CMC) of the cuticle, followed by the inter-macrofibrillar material and/or CMC of the hair cortex to reach macrofibrils [3]. Thus, the narrowness and complexity of this pathway are the cause of the time-consuming penetration. In addition, the high-density disulfide cross-linked structure in the macrofibrils makes it difficult for ingredients to penetrate macrofibrils [4]. Hence, the aromatic sulfonate requires a longer duration to reach the macrofibrils sufficiently. Therefore, achieving a tangible effect is difficult even when the reported curl loosening technology is applied to a rinse-off product such as shampoos with a short usage time.

Therefore, we have developed a technology that enhances the penetration of ingredients, such as the aromatic sulfonate, into the hair fibers and achieves tangible effects, such as curl loosening, in a shorter time. In this study, we focused on the characteristic swelling after applying carbonated water to the hair fibers. This result established that a combination of carbonated water and aromatic sulfonate could improve the curl loosening effect, and the change in the hairstyle was confirmed. Furthermore, structural analysis was performed using tensile stress and small-angle X-ray scattering

(SAXS) measurements to understand the changes within the hair fibers due to the combination of aromatic sulfonate and carbonated water.

2. Materials and Methods

2.1 Hair and keratin powder samples

Chemically untreated Caucasian curly hair was used to evaluate the swelling in carbonated water, the changes in curl loosening and hairstyle, and the penetration amount and depth of *p*-toluene sulfonate (PTS). Additionally, chemically untreated Asian straight hair sample was used for the SAXS and tensile stress measurements to detect small differences accurately. Wool-derived keratin powder was also used to evaluate the swelling in carbonated water.

2.2 Preparation of the solution and shampoo and their carbonation

Carbonated water was prepared by injecting 2.0 % carbon dioxide (CO_2) gas into a sealed aerosol can after pouring water at pH 3.2. PTS was used as an aromatic sulfonate, and a PTS-containing solution was prepared at pH 3.2 by blending 1.1 % of PTS, 4.0 % of benzyl alcohol, 5.0 % of lactic acid, and 10 % of ethanol. In addition, 1.1 % of PTS was added to the shampoo formulation. The PTS-containing solution and PTS-containing shampoo were also carbonated using the procedure similar to that used for the carbonated water.

2.3 Swelling evaluation

Wool-derived keratin powder was immersed in water and carbonated water. The apparent volume of the powders in water was noted as the bulkiness of the keratin powder, which was observed after stirring for 10 s and allowing it to stand for 1 d. The powder was then observed under an optical microscope. The diameter of the dry hair fiber was measured, which was then immersed in water or carbonated water at 40 °C; the diameter was again measured after 5 min. The swelling rate was evaluated based using the following equation (1).

$$\text{Change rate in hair diameter (\%)} = \frac{D_i - D_0}{D_0} \qquad (1)$$

Here, D_0 and D_i indicate the diameter of the hair fiber before and after the treatment, respectively. The average value of 6 samples was calculated.

2.4 Evaluation of hair curl loosening

Curly hair fibers with a curl radius of 0.5–1 cm were cut into a semicircle. The curled shape before the treatment was photographed. Hair fibers were immersed in the PTS-containing solution and shampoo and their carbonated products at 40 °C for 1 or 4 h. After rinsing and drying, the curled shape was photographed again, and the curl-loosening rate was evaluated using the following equation (2).

$$\text{Curl-loosening rate (\%)} = \frac{R_i - R_0}{R_0} \quad (2)$$

Here, R_0 and R_i indicate the curl radius before and after the treatment, respectively. The average value of 9 to 11 samples was calculated.

2.5 Evaluation of the mannequin hair shape

A mannequin for the chemically untreated Caucasian hair was prepared. The hairstyle of the mannequin was photographed after shampoo washing and air-drying. The mannequin hair was washed using the carbonated PTS-containing shampoo. A single washing step included 5 min of hair washing, rinsing, and drying. This step was performed 12 times (a total treatment time of 1 h). After the 6th and the 12th step, the hairstyle of the mannequin was photographed after running fingers through hair several times to break the strongly defined bundle.

2.6 Quantification of the amount of aromatic sulfonate penetration into hair

Hair bundles treated with PTS-containing and carbonated PTS-containing shampoos at 40 °C for 1 h were used for the analysis. Finely chopped hair was dissolved by heating in NaOH solution. The dissolved hair solution was centrifuged at 3000 rpm at 20 °C for 20 min. The centrifuged supernatant was used for liquid chromatography/mass spectrometry (LC/MS) measurement using an LC/MS system manufactured by Agilent Technologies (HPLC: Agilent 1260 Infinity series, MS: Agilent 6130). Unison UK-C18HT was used as an HPLC column, and the mobile phase was flown at 0.2 mL/min by gradiently changing the mixing ratio of 0.1% formic acid-containing water and 0.1% formic acid-containing methanol. Electrospray ionization was used to detect PTS ions found at the negative ion mode. The average PTS penetration amount in hair was obtained by measuring 4 samples.

2.7 Time-of-flight secondary ion mass spectrometry (ToF-SIMS) measurements

Hair fibers treated with PTS-containing or carbonated PTS-containing shampoos at 40 °C for 1 h were used for the time-of-flight secondary ion mass spectrometry (ToF-SIMS) analysis. After hair fibers were embedded in resin, a cross-section of the hair fibers was made. ToF-SIMS IV manufactured by ION-TOF was used for the ToF-SIMS measurement. Negative secondary ions were obtained using a Bi_3^{2+} ion beam as primary ion species, with an acceleration voltage of 25 KV. Primary ions were irradiated in the range of 250 × 250 μm^2, and imaging data were acquired by integrating 50 times. The ratio of the PTS ion intensity compared with the total secondary ion intensity was determined.

2.8 Tensile stress measurements

A 30-mm hair fiber was immersed in water at 40 °C for 1 h, and its tensile stress in water was measured. After drying, the tensile stress of the previously immersed hair was measured in various solutions (the carbonated water, non-carbonated shampoo, and carbonated shampoo) under similar measurement conditions. An MTT680 automated tensile tester manufactured by Dia-Stron Ltd. was used for the tensile stress analysis. The measurement was performed with an upper limit of 2% stretching at 30 mm/min. The change in tensile stress was evaluated based on the average from 10 hair fibers using the following equation (3).

$$\text{Change in tensile stress (\%)} = \frac{mean(S_i) - mean(S_0)}{mean(S_0)} \cdots\cdots \quad (3)$$

Here, S_0 and S_i indicate tensile stress in water and each solution, respectively.

2.9 SAXS measurements

Fifteen hair fibers were bundled and fixed in a sample holder, which was then immersed in water at 40 °C for 1 h. After drying, the SAXS measurement was performed. Subsequently, the sample holder with the hair bundle was immersed in various shampoo solutions (basic, PTS-containing, and carbonated PTS-containing shampoos) at 40 °C for 1 h. After rinsing and drying, the SAXS measurement was performed again. Nano-viewer manufactured by Rigaku Co., Ltd., was used for the SAXS measurement. The hair bundle was irradiated with X-rays for 4 h under the conditions of 1.5418 Å (Cu-Kα) wavelength, 40 kV tube voltage, 30 mA tube current, and 645.5 mm camera length. The average distance between the intermediate filaments (IFs) (A_m) within the macrofibrils of 15 hair fibers was obtained, and the change rate in A_m was evaluated using the following equation (4).

$$\text{Change rate in } A_m\ (\%) = \frac{A_i - A_0}{A_0} \qquad (4)$$

Here, A_0 and A_i indicate the distance before shampoo treatment and after each shampoo treatment, respectively.

3. Results and Discussion

3.1 Curl loosening function of *p*-toluene sulfonate

Figure 1 shows the change in the hair curl radius of the hair fiber before and after the treatment with PTS solution. An immersion time of 4 h was required to increase the curl radius by 20 %, which is equivalent to 48 individual shampoo washings for 5 min. This required time is lengthy, making it difficult for consumers to realize the tangible effect.

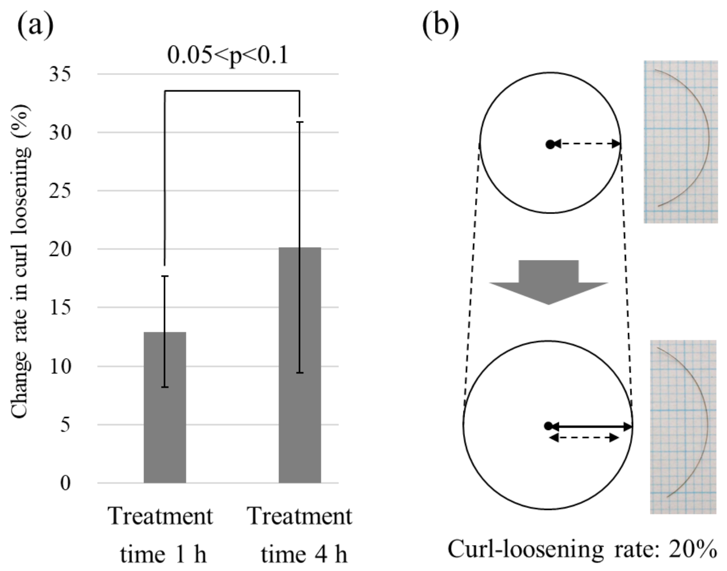

Figure 1. (a) Changes in curl loosening of a curly hair fiber treated with *p*-toluene sulfonate (PTS)-containing solution. Data of (a) presented as mean ± standard deviation of results of 10 samples, and Student's t-test was performed to confirm the statistically significant differences. (b) Schematic diagram of the curl-loosening rate, and a photograph of a typical curly hair fiber used in this evaluation.

3.2 Swelling effect of carbonated water

A technology that enhances the penetration of PTS has been developed to solve the issue of low penetration. Organic solvents, acids, and alkalizing agents are generally used as penetration-enhancing ingredients. In this study, we focused on the effect of carbonated water at low pH containing CO_2 and carbonic acid, which is an acid with a molecule structure smaller than that of the general penetration-enhancing ingredients [5].

In Europe, hot springs containing carbonated water have been traditionally used for medical skin treatment. In cosmetics, CO_2 in carbonated water is known to moisturize the skin and improve its appearance [6]. Carbonated water has also been reported to enhance the transdermal absorption of other ingredients into the skin [7]. Because carbonated water has various effects, it can also affect hair. Therefore, we studied the basic effect of carbonated water on the hair fibers and the possible penetration enhancement of the aromatic sulfonate. Figure 2-a illustrates the changes in the keratin powder, which was immersed in water and carbonated water. The bulkiness of the keratin powder in the carbonated water significantly increased compared to that of the keratin powder in water. When keratin powder particles were magnified using an optical microscope, the particles in the carbonated water demonstrated increased diameter. This result indicates the swelling of keratin by the carbonated water. Figure 2-b shows the changes in the diameter of the hair fiber, which was immersed in water and carbonated water. The hair fiber diameter in the carbonated water was further increased compared to that in water. Thus, the carbonated water significantly swells the hair and can potentially expand the penetration pathway within the hair fibers.

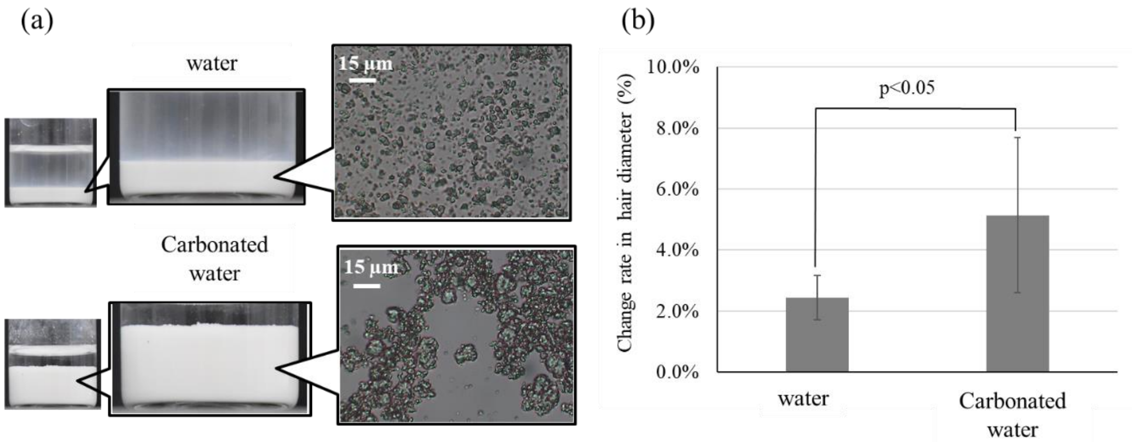

Figure 2. Evaluation of swelling in (a) keratin powder and (b) hair fiber. Data of (b) presented as mean ± standard deviation of results of 6 samples. Student's t-test was performed to confirm the statistically significant differences.

3.3 Promotion effect of carbonated water in hair curl-loosening function

Based on the results that carbonated water promoted hair swelling, the possibility of improving the effect of PTS was studied. Figure 3 illustrates the results of the hair fibers treated using carbonated PTS solution and carbonated water in addition to Figure 1. The curl radius of the hair fiber treated with the PTS solution for 1 h increased to 13 %. In contrast, the curl radius of the hair fiber that was treated with the carbonated PTS solution for 1 h increased to 20 %. This result indicates the similar change that treated with the PTS solution for 4 h, the functional time of curl loosening technology can be shortened to 1/4. In addition, the hair fiber treated using only carbonated water did not loosen the curl. Therefore, we considered that carbonated water itself did not exhibit the curl loosening effect and contributed to the promotion of the curl loosening effect of PTS.

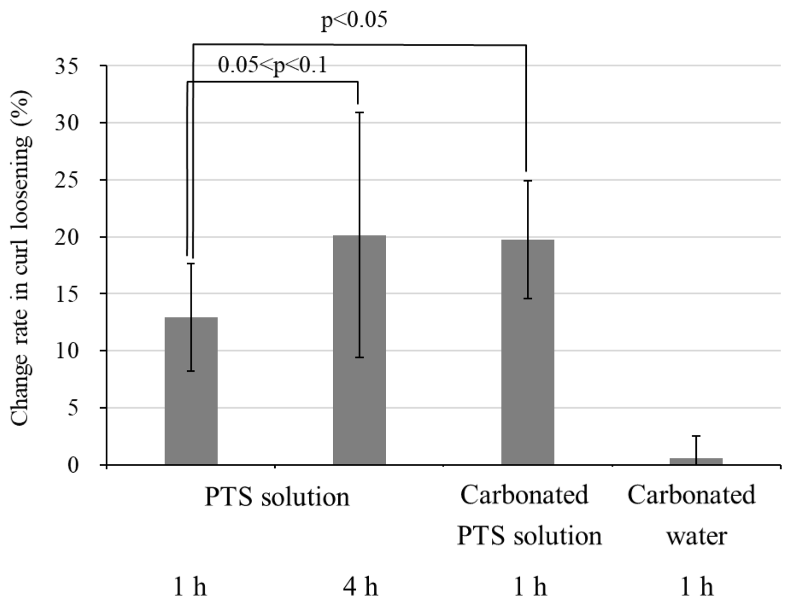

Figure 3. Changes in curl loosening of curly hair fibers treated with PTS solutions (carbonated PTS solution: n=11; other results: n=10). Data presented as mean ± standard deviation. Student's t-test was performed to confirm the statistically significant differences.

Figure 4 shows the promotion effect of carbonated water using the shampoo formulation. Compared to the hair fibers treated using the basic shampoo formulation, the PTS-containing shampoo increased the curl-loosening rate. In addition, the effect of the carbonated PTS-containing shampoo tended to increase further. This result suggests that carbonated water effectively enhances the function of PTS even in the shampoo formulation.

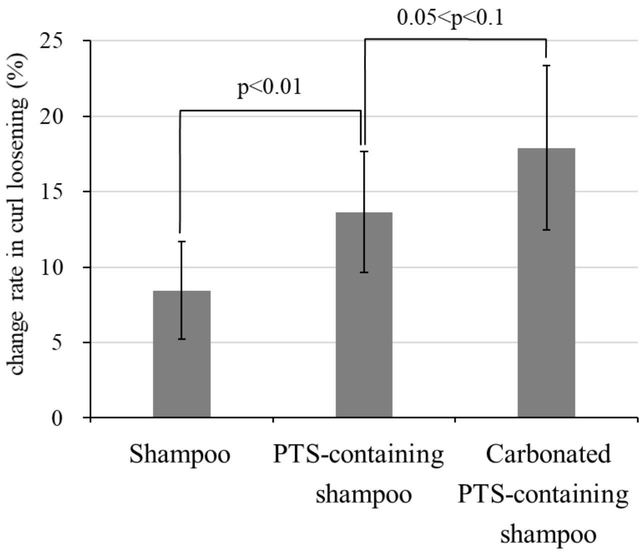

Figure 4. Changes in the curl loosening of curly hair fibers treated with each type of shampoo (carbonated PTS-containing shampoo: n=9; other results: n=10). Data presented as mean ± standard deviation. Student's t-test was performed to confirm the statistically significant differences.

The change in the style of the hair bundle, which is close to real hair condition, was also evaluated. The curly hair was washed using the carbonated PTS-containing shampoo. Figure 5 shows the photographs of the mannequin before the treatment, after washing 6 times, and after washing 12 times. Repeated washings loosened the hair curls of the mannequin, visibly changing the hairstyle. Moreover, the loosening of the curls resulted in the alignment of the curl shape, forming a well-ordered line. It is remarkable to achieve such changes through usual hair washing using only the rinse-off product.

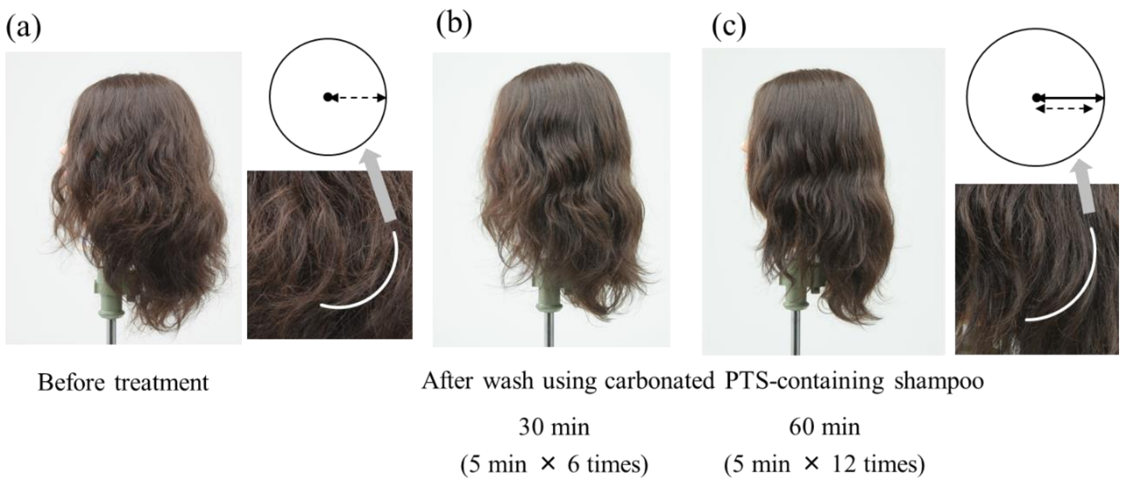

Figure 5. Evaluation of the mannequin hairstyle (a) before treatment and (b, c) after wash using carbonated PTS-containing shampoo (b: washing for a total of 30 min; c: washing for a total of 60 min). Figures 5-a and c include enlarged photograph and schematic diagrams showing changes in the curl lines.

3.4 Effects of carbonated PTS-containing formulation on internal structure of hair fiber

Carbonation of PTS-containing formulation promotes the hair curl-loosening effect. This result suggests the possibility that carbonic acid in the carbonated water has widened the penetration pathway in the hair fibers and changed the penetration amount and penetration depth of PTS. Therefore, the penetration amount and penetration depth of PTS were analyzed using LC/MS and ToF-SIMS, respectively; the results are shown in Figure 6. Contrary to expectations, the penetration amount of the carbonated PTS-containing shampoo-treated hair did not increase compared to that of the PTS-containing shampoo-treated hair (Figure 6-a). Moreover, the penetration depth of PTS inside the hair fiber did not change sufficiently because the PTS-containing shampoo-treated hair fiber was already penetrated PTS with sufficient depth (Figure 6-b). Thus, the carbonation of the PTS-containing formulation may have affected the penetration inside the microstructure that cannot be distinguished by the penetration amount of PTS detected in the entire hair fiber and the imaging analysis. Hence, we analyzed the structural changes in the macrofibrils using the tensile stress and SAXS measurement as the aromatic sulfonate reportedly affected the structure in the macrofibrils [1,2].

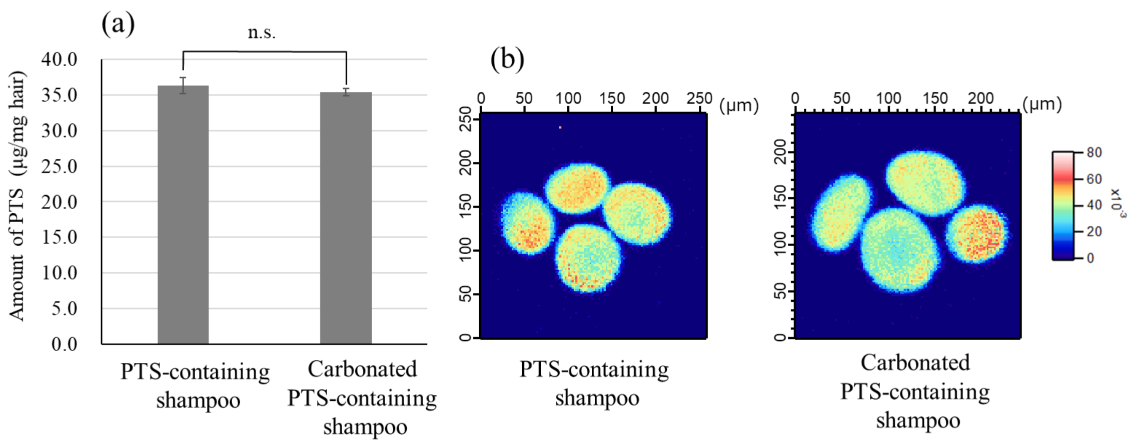

Figure 6. (a) Quantitative result of PTS using liquid chromatography/mass spectrometry and (b) time-of-flight secondary ion mass spectrometry results of the cross-sectional area of hair fibers. Hair samples treated with non-carbonated and carbonated PTS-containing shampoos were used in each result. Data of (a) presented as the mean ± standard deviation of results of 4 samples. Student's t-test was performed to confirm the statistically significant differences. Results of (b) show PTS ion image standardized by the total ion image.

A tensile stress of up to 2% in water reportedly contributes to the mechanical properties of IFs and keratin-associated proteins (KAPs) that compose the macrofibrils [8,9]. Therefore, the tensile stress was measured to understand the ability of the carbonated water from the viewpoint of the mechanical properties of the macrofibrils. Figure 7 illustrates the change in the tensile stress of the hair fibers immersed in different solutions compared to that of the same hair fiber immersed in water. The tensile stress results in the carbonated water and carbonated shampoo were lower than that in water and non-carbonated shampoo, respectively. Therefore, it is assumed that carbonic acid in the carbonated water can penetrate up to IFs and KAPs inside the macrofibrils, making them more flexible.

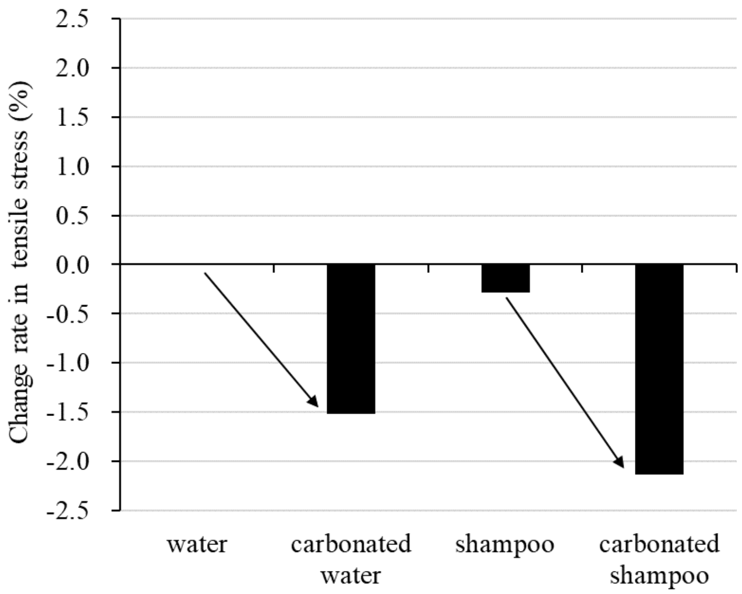

Figure 7. Changes in the tensile stress of the hair fibers in each solution compared to that in water

Considering the tensile stress results on the flexibility of macrofibrils, carbonic acid may enhance the penetration of PTS into the macrofibrils and swell them. Therefore, SAXS measurement was performed to analyze the change in the nano-level structure with the swelling of the macrofibrils. Figure 8 illustrates the SAXS analysis result. A scattering pattern, as shown in Figure 8-a, is observed in the SAXS measurement of the hair bundle. Figure 8-b demonstrates the one-dimensional result of the equatorial direction in Figure 8-a. The broad peak detected near q = 0.7 nm^{-1} indicated the spacing (A_m) between the IFs within the macrofibril. This result provides information on the sum of the occupancy distance of KAPs, which fill between the IFs and the radius of IF [10,11,12]. Figure 8-c illustrates the change in the A_m before and after each shampoo treatment. The A_m of the hair bundle treated with the basic shampoo formulation was slightly increased. However, the hair bundle treated with the PTS-containing shampoo had a wider A_m than that of the hair bundle treated with the basic shampoo. In addition, the hair bundle treated with the carbonated PTS-containing shampoo exhibited more widened A_m. This change in A_m is largely influenced by the globular KAPs that swell isotopically [13].

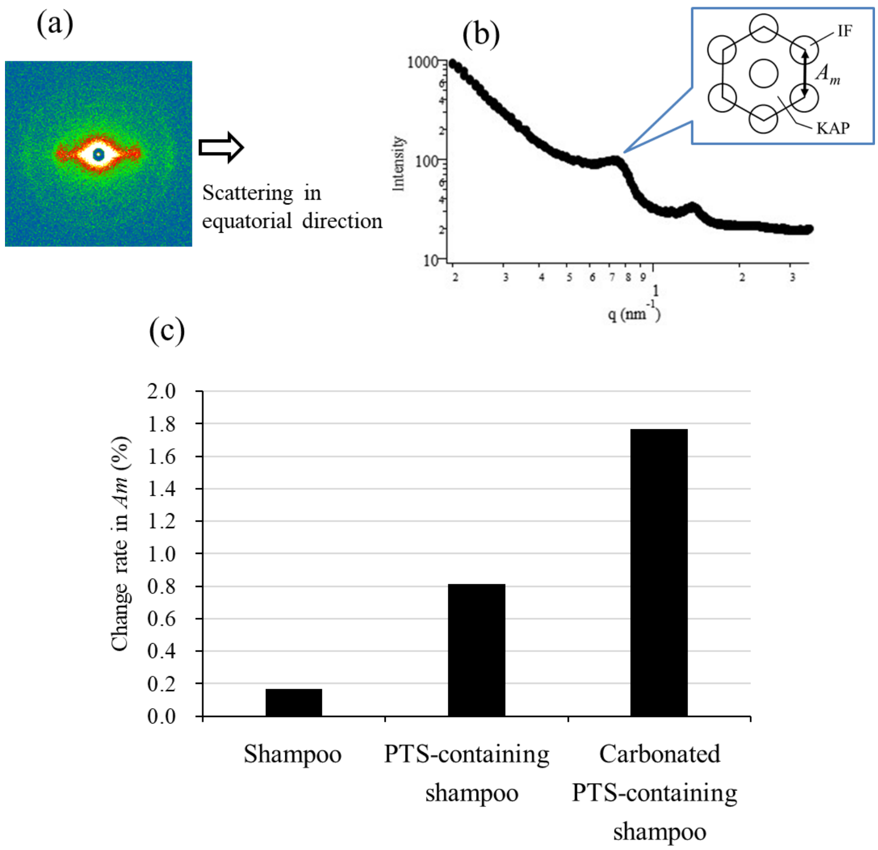

Figure 8. (a) Typical scattering patterns obtained from the small-angle X-ray scattering analysis of the bundle of 15 hair fibers. (b) One-dimensional equatorial intensity profiles extracted from Fig.8-a. (c) Changes in the spacing between IFs (A_m) of the hair bundle treated using each type of shampoo.

Figure 9 shows the hypothetical diagram of the loosening of curly hair fibers by PTS and carbonated water. The curly hair fibers have helical- and parallel-arranged IFs in the ortho-like and para-like cortex dominating the convex and concave sides, respectively [1,2]. When the aromatic sulfonate treatment swells the curly hair fibers laterally, the IFs of the convex half side contract longitudinally greater than that of the concave half side [1,2]. The difference in the contraction in the fiber axis direction between the concave and convex sides loosens the curls. Further swelling of the KAPs around the IFs and the sufficient reach of the aromatic sulfonate to IFs increase the tilt of the helical IFs in the ortho-like cortex. Thus, we consider that carbonic acid in the carbonated PTS-containing formulation promotes the swelling of the KAPs and makes more PTS reach IFs.

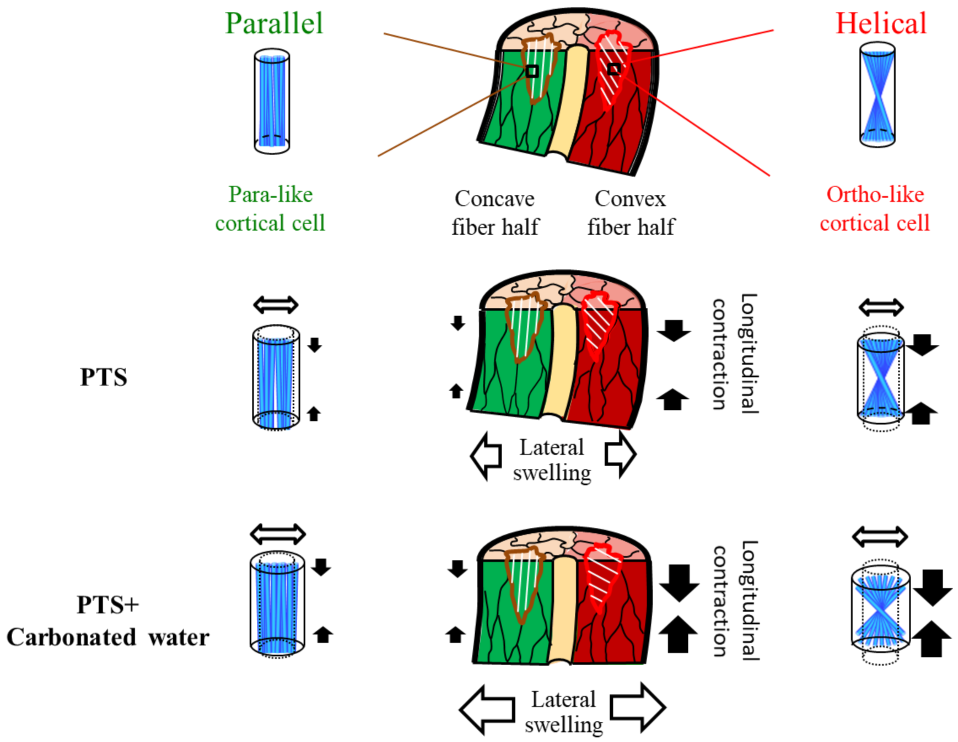

Figure 9. Hypothetical diagram of the loosening of curly hair fibers by PTS and carbonated water. The para-like cells are located in the concave fiber half and contain parallel IF arrangements, while ortho-like cells are located in convex fiber half and contain helical IF arrangements [1,2]. When PTS swells the hair fibers laterally (increase in the A_m, as shown in Figure 8-c), the helical IFs in the convex side tilt and contract more in the longitudinal direction than in the parallel IFs in the concave side. Carbonated water extends this mechanism based on promoting the swelling of the KAPs and making more PTS reach IFs. The greater longitudinal contraction of the cortex in the convex fiber half causes the curly hair fibers to loosen.

Thus, carbonic acid can facilitate the penetration of PTS into the KAPs, which have a high-density disulfide cross-linked structure, based on the ability of making the structure in the macrofibrils flexible. Even when the PTS penetration amount detected in the entire hair fiber does not increase, it is assumed that this function further swells the KAPs, makes more PTS reach IFs, and enhances the curl-loosening effect.

4. Conclusion

Low penetration performance is a major issue for hair care ingredients that internally affect the hair fibers. Therefore, enhancing the penetration of the hair care ingredients is important. The damage-less curl-loosening technology using an aromatic sulfonate such as PTS requires a longer duration to achieve tangible effects. Therefore, to solve this issue, we have developed a technology for enhancing the penetration of PTS based on the results that carbonated water promoted hair fiber swelling. Contrary to expectations, carbonated water did not change the total amount of PTS penetration into the hair. However, we consider that the carbonic acid can facilitate the penetration of PTS into the KAPs, which have a high-density disulfide cross-linked structure, based on the ability of making the structure in the macrofibrils flexible. Even when the PTS penetration amount detected in the entire hair fiber does not increase, this function can make more PTS reach IFs and enhance the loosening of the curls. The carbonated PTS-containing shampoo also changed the hairstyle of the mannequin hair. Thus, the developed technology can introduce the concept of stress-free styling with usual hair washing behavior. This shampoo formulation is promising and may transform the world of rinse-off products. Moreover, the above results suggest that carbonated water can enhance the penetration performance of various hair care ingredients other than aromatic sulfonates, which control the shape, color, and texture.

Conflict of Interest Statement. NONE.

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