

## Article

## Natural 'Green' Sugar-Based Treatment for Hair Styling

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**Abstract:** A major drawback of current hair styling treatments is their use of toxic chemicals, such as thioglycolates, sulfites, formaldehyde, and others. Exposure to such chemicals is not only harmful to hairstylists but also to the millions who routinely receive hair treatments. The present research discusses the development of a benign sucrose-based crosslinker consisting of aldehyde groups to stabilize hair via crosslinking amine groups in keratin. ATR-FTIR and  $^1\text{H}$ -NMR were used to confirm functional groups on sucrose. Hair straightening was carried out by crosslinking via flat ironing. Crosslinked hair swatches were hung in a high humidity environment and subjected to repeated washings with shampoo to characterize the permanency of the treatment. Hair straightening through crosslinking was found to be durable to high humidity and repeat shampoo washings. The tensile characteristics of hair, such as fracture stress, strain, and Young's modulus, were unaffected by the treatment. SEM images showed no damage to surface scales. The sucrose-based crosslinker could be used to create curls in straight hair as well.

**Keywords:** keratin; oxidized sucrose; hair styling; sucrose tetra-aldehyde; Schiff's base reaction



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## 1. Introduction

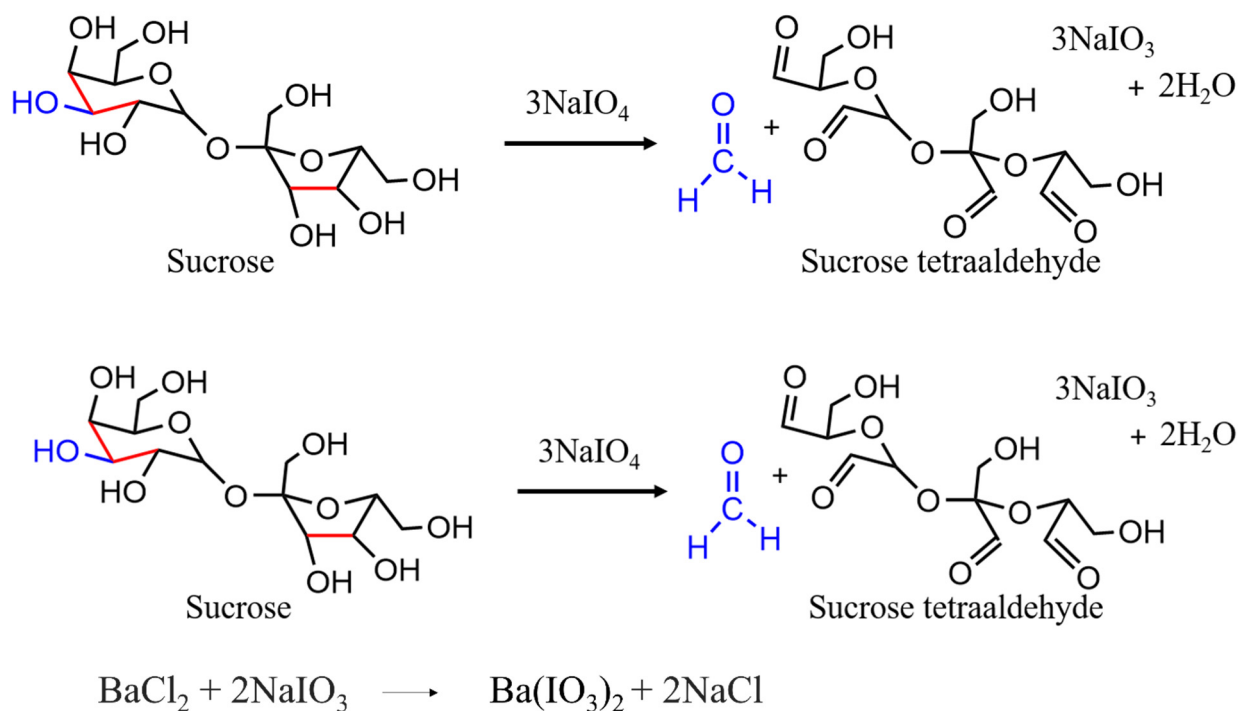
The haircare industry has seen rapid growth in the past couple of decades, and so have the number of products associated with haircare [1]. Hair styling is a major part of haircare and involves grooming the hair to achieve more manageable and frizz-free hair [2]. Hair straightening treatments are in vogue and require both chemical and heat treatments to achieve both temporary and permanent hair straightening to obtain versatile hair styles [2]. Human hair is made up of keratin, a protein that consists of amino acids linked by polypeptide bonds [3–5]. Polypeptide molecules form alpha-helix structures, which are twisted together to form microfibrils and many such microfibrils, together, form a macrofibril [4]. The inner part of hair is called the cortex and is made up of cortical cells that contain macrofibrils, which contribute to the strength, color, and texture of hair [4]. The cortex is known to form about 75% of hair volume [6]. The outer layer of hair, called the cuticle, consists of scales that act as a preventive barrier for the cortex and, thus, protect the hair [4,5].

A variety of treatments for hair straightening are presently commercially available. Altering the cortex is considered important for straightening hair [5,7,8]. The most common method used for hair straightening is flat ironing [6]. Flat ironing involves alterations to hydrogen bonds and salt linkages within the cortex through heat and mechanical stress [6]; however, flat ironing only manages to straighten hair temporarily, and it can return to its original curly state when exposed to high humidity or washing. Hair rebonding or chemical straightening are other methods used to obtain more permanent straightening. In these processes, strong chemical relaxers or reducing agents are used to break the disulfide bonds in the hair structure; following this, neutralizers or oxidizing agents are used to rebond the structure again. Permanent straightening is generally achieved through modifying covalent bonds. The relaxers used for breaking these bonds are generally strong and alkaline in nature and can be hydroxide-based (~pH 13) or thio-based (~pH 10) [9]. Sodium hydroxide (lye-based) solution (3.5%) or guanidine hydroxide activated with 4–7% calcium hydroxide,

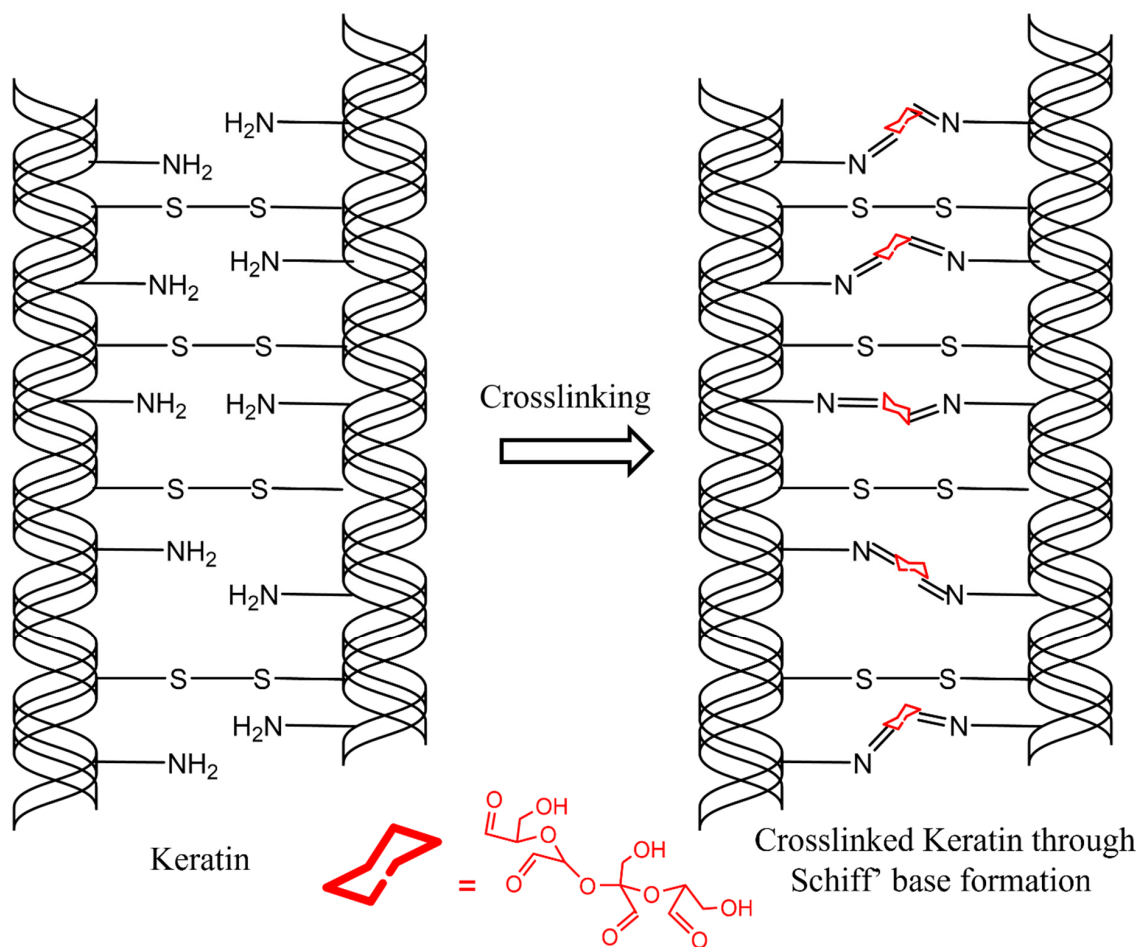
potassium hydroxide, or lithium hydroxide (non-lye based) alkaline straighteners are commonly used, in which the sulfur atom from a disulfide bond is removed and converted into a lanthionine bond, creating permanent, non-reversible straightness [6]. Thio-based chemicals, such as ammonium or ethanolamine thioglycolate, and sulfites are commonly used as reducing agents for hair. These chemicals convert disulfide bonds to sulfhydryl groups (chemical reduction), which are further oxidized to re-form disulfide bonds at the desired locations to obtain the needed hair (straighter) conformation [10,11]. Both hydroxide-based lanthionization and thio-based reduction and oxidation techniques are known to damage and weaken hair permanently as they alter the cystine content or the disulfide bonds in the cortex and hydrolyze peptide bonds [6,9]. These also require a great number of after-hair-care measures and result in thinning hair and dullness in the long run. These chemicals have strong odors and can be irritating to the lungs, skin of the head, or eyes during application. Thioglycolate and ammonium thioglycolate, which are toxic and carcinogenic, can be harmful if they come into contact with skin [9,10]. In addition, the hydroxide and thio-based straighteners, formaldehyde and glutaraldehyde, have been actively used for hair straightening, despite having been banned due to their toxicity, simply because they are inexpensive and result in shiny, straight hair through the crosslinking of the amine groups in the keratin [6]. Formaldehyde is even more dangerous compared to glutaraldehyde as it causes serious damage to tissues and the respiratory tract of users, as well as those of the hairdressers working in salons, and has been classified as a carcinogen [6,9,12].

There have been some attempts to use non-toxic reducing agents to break the disulfide bond in keratin and re-form them to attain straightness. The use of cysteine as a 'green' reducing agent and the use of polycarboxylic acids, such as citric acid, butane tetracarboxylic acid (BTCA), malic acid, and others, to crosslink hair have been studied [2,13–15]. However, all these are two-step processes that still involve the reduction step (breaking the disulfide bonds), which permanently affects the strength of hair. A concise review of various hair straightening methods and their adverse effects on hair structure and properties, as well as on the skin, was presented by Barreto et al. [16]. Details of hair damage, in terms of their porosity and cysteic acid content after chemical hair straightening, were provided by Sedik et al. [17].

The present research discusses the development of a sucrose-based nontoxic keratin crosslinker that can straighten hair effectively. Sucrose was oxidized using sodium periodate to form sucrose tetraaldehyde (ST), as shown in Scheme 1. The four aldehyde groups created on sucrose after oxidation can react with the amine groups present in keratin molecules in hair, forming covalent crosslinks within the keratin. Crosslinking of keratin in hair through Schiff's base formation is shown in Scheme 2. The crosslinking reaction stabilizes hair by forming a 3D network, and, when straightened using a flat iron, the crosslinking reaction is completed, which retains hair straightness. The effect of ST hair treatment on the durability of the straightness after exposure to high-humidity conditions and repeated shampoo washing was studied. Natural Brazilian curly hair was used in this straightening study; however, any other hair with the same keratin chemistry can be expected to perform similarly. Alternatively, this innovative green natural hair styling crosslinker could also be used to create curls in straight hair.



**Scheme 1.** Oxidation reaction of sucrose forming sucrose tetraaldehyde.



**Scheme 2.** Crosslinking of keratin in hair through Schiff's base formation.

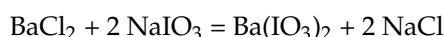
## 2. Experimental

### 2.1. Materials

One-hundred percent virgin Brazilian natural curly human hair (7.5" curly length; 12" stretched length) sample was obtained from the Amazon. A Remington® flat iron with settings from 10 to 30 and Pantene® shampoo were purchased from a local Target Store. Sodium periodate ( $\text{NaIO}_4$ )  $\geq 99\%$  and barium dichloride ( $\text{BaCl}_2$ ) were purchased from Acros Organics, Bound Brook, NJ, USA and VWR, Rochester, NY, USA, respectively. Sucrose powder and sodium hydroxide ( $\text{NaOH}$ ) pellets were purchased from Sigma-Aldrich Chemical Co., Allentown, PA, USA.

### 2.2. Preparation of Sucrose Tetraaldehyde Solution for Hair Treatment

5 grams (g) of sucrose was dissolved in 100 mL of DI water. 6 g of  $\text{NaIO}_4$  was added to the sucrose solution. Oxidation was carried out in the complete dark at room temperature (RT) for 16 h with gentle stirring at 200 rpm. At the end of 16 h, after achieving the required oxidation, 4 g of  $\text{BaCl}_2$  was added to the solution to stop further oxidation.  $\text{BaCl}_2$  reacts with  $\text{NaIO}_3$  to form  $\text{Ba}(\text{IO}_3)_2$ , which is insoluble in water at lower temperatures. The reaction is shown below. After adding  $\text{BaCl}_2$ , the solution was stirred for 5 min and placed in the refrigerator for 1 h to allow precipitation of  $\text{Ba}(\text{IO}_3)_2$ . Once fully settled, the solution was filtered to separate the insolubilized  $\text{Ba}(\text{IO}_3)_2$  from ST. At this time, the pH of the ST solution was observed to be around 3.5. The pH of the ST solution was adjusted to 7 using  $\text{NaOH}$  before the hair treatment.



### 2.3. Characterization of Sucrose Tetraaldehyde (ST) Solution

The prepared ST solution was characterized using attenuated total reflection-infrared spectroscopy (ATR-FTIR) and proton nuclear magnetic resonance ( $^1\text{H}$ -NMR) to analyze the functional chemical groups. The ATR-FTIR spectra were collected using a Thermo Nicolet Magna-IR 560 spectrometer (Madison, WI) having a split pea accessory. Each scan was an average of 300 scans from  $4000 \text{ cm}^{-1}$  to  $500 \text{ cm}^{-1}$  wavenumbers.  $^1\text{H}$  NMR spectra were recorded on an INOVA 400 spectrometer (Varian Inc., Palo Alto, CA, USA) using  $\text{D}_2\text{O}$  as a solvent.

### 2.4. Hair Straightening Treatment

A swatch of hair (7.5" in curly length and weighing 1.2 g) was washed with shampoo and air dried before the treatment. The washed swatch of hair was clamped onto an aluminum foil using a clip, and the prepared ST solution was applied onto the curly hair using a hair dye brush. A hair dye brush was dipped in the ST solution, and smaller sections of hair were individually coated with ST solution from top to bottom, using 3–4 brush strokes of about 2 inches in length. The brush was dipped in ST solution multiple times and spread onto the hair to ensure that all the hair in the swatch was completely wet and coated with the solution from all sides. The hair swatch was then allowed to dry for about 8 min, allowing the ST solution to diffuse into the hair before crosslinking the hair using a flat iron. The drying step avoids hair damage from wet flat ironing, which reduces the hair's strength. Hair was slowly flat ironed with about 8 passes at the flat iron setting of 25, which corresponded to  $180^\circ\text{C}$ . A flat iron with settings of 15, 20, 25, and 30 was used for straightening the hair. Flat iron settings of 15 and 20 required a higher number of passes to straighten the hair. The hair straightening setting on the flat iron was optimized to 25 to minimize the number of passes required for straightening the hair using sucrose tetraaldehyde to avoid damage to hair due to heat. The flat iron setting of 30 corresponds to  $215^\circ\text{C}$ . ST solution was applied to the hair a second time, dried, and flat ironed, as mentioned above. The straightened hair swatch was set aside for 10 min at RT before washing off with tap water at RT to remove excess crosslinker present on the surface and flat ironed again for another 4–5 passes if the hair curls after washing. ST solution-treated

hair is termed STA. Another swatch of hair was washed with shampoo, air-dried, and flat-ironed at the iron setting of 25 for 25–30 passes until straight without using the ST solution. This swatch is termed flat iron (FI).

### 3. Characterization of Hair

Since humidity affects the straightness and curliness of the hair, most of the hair characterization techniques were performed in a conditioning room maintained at standard ASTM conditions of 21 °C and 65% relative humidity (RH). The untreated control (C), FI and STA hair swatches were hung in the conditioning room (21 °C and 65% RH) at the same time for up to 45 days, and pictures were taken at predetermined time intervals to observe the effect of humidity on the hair straightness.

A set of hair swatches containing C, FI, and STA specimens was washed with shampoo every two days and hung in the conditioning room in between washes, and pictures were taken after washing, drying, and two days after washing to mimic the real-life application. The straightening efficiency (SE) for FI and STA hair specimens was calculated after measuring their lengths before and after treatments using a ruler and using the formula given by Equation (1) [9]. At the same time, the number of curls (twists) in the hair was also observed.

$$\text{Straightening efficiency (\%)} = 100 - \left( \frac{\frac{\text{number of twists after treatment}}{\text{length of hair after treatment}}}{\frac{\text{number of twists before treatment}}{\text{length of hair before treatment}}} \right) \times 100 \quad (1)$$

SE values were also calculated for C, FI, and STA hair swatches as a function of days of exposure in the conditioning room at 21 °C and 65% RH for up to 45 days.

The tensile properties of the hair were characterized using an Instron universal testing machine, model 5566 (Instron Corp., Canton, MA, USA). Individual hair specimens from various C, FI, and STA swatches were mounted on rectangular paper tabs by securing the two ends with a self-adhesive tape (3M Corp., Minneapolis, MN, USA). The diameter of each hair was measured using a calibrated optical microscope, Olympus, model BX51 (Melville, NY, USA), at three different locations, and the average was used to calculate the tensile properties of individual hair. The hair specimens were conditioned at 21 °C and 65% RH for 3 days prior to testing. The tensile tests were conducted at  $65 \pm 3\%$  RH and  $21 \pm 1$  °C using a gauge length of 30 mm and a strain rate of  $0.6 \text{ min}^{-1}$ . Thirty single hair specimens were randomly chosen from the top, middle, and bottom parts of the swatches of each type (C, FI and STA) for testing and statistical analysis. For the FI and STA hair, 10 specimens were chosen from each of the three different swatches treated at different times using sucrose tetraaldehyde solutions prepared at different times to ensure reproducibility of the results.

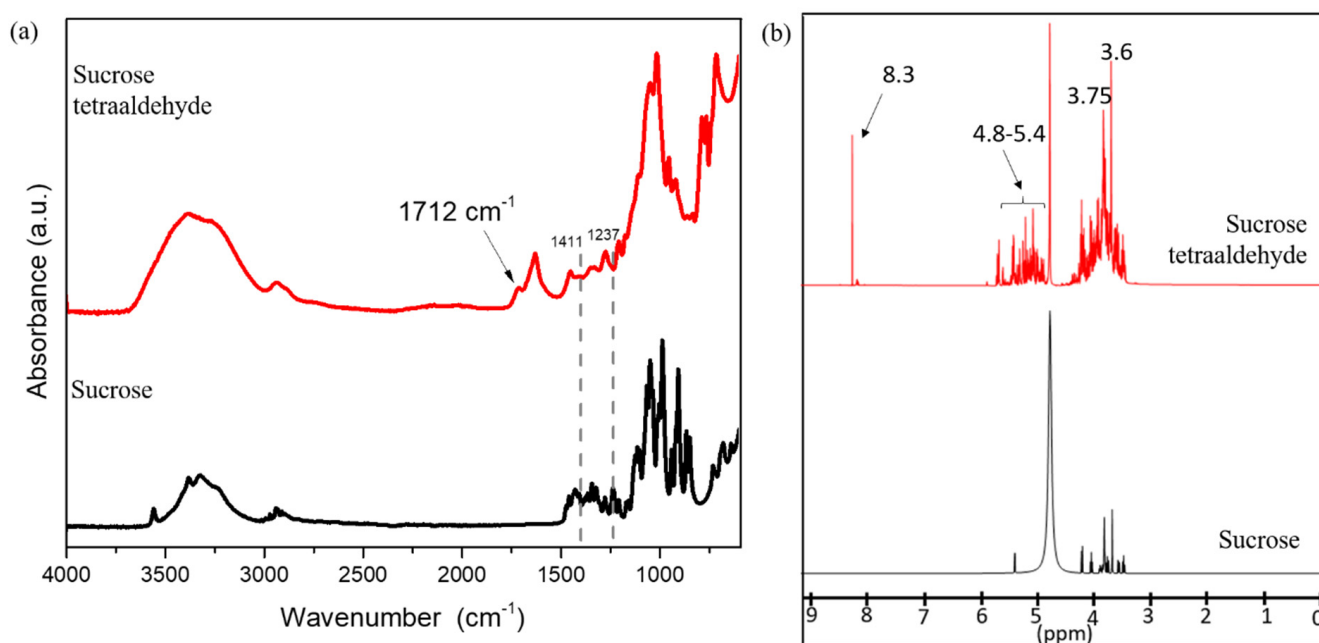
Surface characterization of the C, FI, and STA hair was performed using a Zeiss Gemini 500 scanning electron microscope (Germany) at 1 kV.

## 4. Results and Discussion

### 4.1. Characterization of Sucrose Tetraaldehyde Solution

Figure 1 shows ATR-FTIR and  $^1\text{H}$ -NMR spectra of sucrose and the prepared ST solution. As can be seen in Figure 1a, the ATR-FTIR spectrum for sucrose shows unique peaks associated with sucrose in the fingerprint region between  $1500 \text{ cm}^{-1}$  and  $700 \text{ cm}^{-1}$  wavenumbers. The peak observed at  $907 \text{ cm}^{-1}$  corresponds to the C-H bending in sucrose. The peaks at  $1049 \text{ cm}^{-1}$  and  $1237 \text{ cm}^{-1}$  correspond to the C-O stretch and C-C stretch in sucrose from C-OH groups, respectively, while the peak at  $1003 \text{ cm}^{-1}$  corresponds to the stretching of the C-O band of the C-O-C linkage [18]. The peaks at  $1322 \text{ cm}^{-1}$  and  $1411 \text{ cm}^{-1}$  are due to O-H bending of C-OH groups in sucrose. As seen in the spectrum of ST in Figure 1a, the peak at  $1237 \text{ cm}^{-1}$  disappeared, and the intensity of the peak at  $1411 \text{ cm}^{-1}$  reduced. Both these peaks correspond to the C-OH bending in sucrose, and the reduction in

the peak intensity is the result of the oxidation of hydroxyls to aldehyde groups. The ATR-FTIR spectra of ST showed an additional peak at  $1712\text{ cm}^{-1}$ . This new peak at  $1712\text{ cm}^{-1}$  lies in the carbonyl region and corresponds to the aldehyde groups resulting from sucrose oxidation [18,19].  $\text{NaIO}_4$  has been shown to cleave the vicinal hydroxyl groups showed by red color bonds in Scheme 1 and attach  $\text{IO}_4^-$  onto the hydroxyl groups [20–22]. The lone pair on OH then attacks the iodine and initiates the proton transfer. At the same time, the lone pair from the adjacent hydroxyl group attacks the same iodine, leading to two proton transfers, which causes the oxidation of hydroxyl groups to aldehyde groups. As seen from the structure of sucrose in Scheme 1, fructose has only two vicinal hydroxyl groups that  $\text{IO}_4^-$  can attach to and initiate proton transfer from two hydroxyl groups oxidizing them to two aldehyde groups and leaving  $\text{NaIO}_3^-$  and  $\text{H}_2\text{O}$  [20]. Glucose has three such vicinal hydroxyl groups, and  $\text{IO}_4^-$  cleaves one pair of hydroxyl groups shown in red color bonds and initiates proton transfer. Another  $\text{IO}_4^-$  attaches to the second red color bond shown in Scheme 1 and initiates the proton transfer. The middle hydroxyl group shown in blue color is released as formaldehyde, as shown in Scheme 1, leaving behind  $2\text{NaIO}_3^-$  and  $\text{H}_2\text{O}$ . Thus, overall, five secondary hydroxyl groups that lie in the vicinity of each other result in four aldehyde groups creating sucrose tetraaldehyde (ST). This confirms earlier results obtained by Xu et al. [22]. A similar peak at  $1718\text{ cm}^{-1}$  was also seen by Jalaja and James after oxidizing sucrose using  $\text{NaIO}_4$  [20]. In both spectra obtained for sucrose and the ST solution, the peak observed around  $3360\text{ cm}^{-1}$  corresponds to hydroxyl groups in sucrose, and the peaks between  $2900$  and  $2700\text{ cm}^{-1}$  correspond to the C-H stretch. The additional peak at  $1630\text{ cm}^{-1}$  in ST is from the hydroxyl groups of water.



**Figure 1.** (a) ATR-FTIR and (b)  $^1\text{H}$ -NMR spectra of sucrose and sucrose tetraaldehyde.

Figure 1b shows  $^1\text{H}$ -NMR spectra for sucrose and ST. The protons associated with sucrose were seen at 5.4 ppm and between 4.2 ppm and 3.2 ppm. The proton shift seen at 4.7 ppm in both spectra is a result of the  $\text{D}_2\text{O}$  used as a solvent. The proton shifts at 4 ppm and 4.2 ppm in the sucrose spectrum were due to the protons from secondary hydroxyl groups present on the fructose ring in sucrose. The three proton shifts associated with the three secondary hydroxyl groups on the glucose molecule are seen between 3.5 and 3.75 ppm in the sucrose spectrum. Fructose and glucose have two and three vicinal hydroxyl groups or secondary hydroxyl groups, respectively, which are cleaved by  $\text{NaIO}_4$  and oxidized to form two aldehyde groups on each fructose and glucose (as discussed above and in reaction Scheme 1). Comparing the intensities of the two strong proton



shifts at 3.6 and 3.75 in sucrose and ST, the intensity of the proton shift at 3.75 reduced significantly relative to the intensity of proton shift at 3.6 ppm in sucrose tetraaldehyde. While both proton shifts at 3.6 and 3.75 are due to the secondary protons, the proton shift at 3.75 ppm corresponds to the proton attached to the carbon present at the center of the three hydroxyl groups in glucose (shown in blue color in Scheme 1). The lower intensity of proton shift at 3.75 ppm relative to the proton shift at 3.6 ppm, indeed, shows that the  $\text{NaIO}_4$  successfully cleaved the vicinal hydroxyl groups and the proton attached to the center carbon of the two bonds shown in red color in Scheme 1 is lost due to the attack. The aldehyde group formation can be clearly seen from the  $^1\text{H-NMR}$  of ST, where an additional proton shift was observed at 8.3 ppm due to the protons associated with the aldehyde groups created by oxidation [19]. The additional proton shifts between 4.8 and 5.5 ppm indicate the intermolecular acetal protons due to the hemiacetal formation [19–22]. These results confirm earlier results by de Witt et al., who observed sucrose tetraaldehyde formation using the HPLC method [23].

#### 4.2. Characterization of Hair

Figure 2 shows pictures of control (C), flat ironed (FI), and ST solution-treated (STA) hair swatches, from left to right, respectively, taken from day 0 to day 15 exposure in the conditioning room after the treatments. As seen in Figure 2a, the control hair swatch showed five curls (each curl is counted as a 'z' from top to bottom). It is clear that flat ironing helps to straighten the curls, as seen in Figure 2a (0 day), and so does the STA treatment. As can be seen in Figure 2b, however, the FI hair showed at least one curl at the bottom of the swatch after just 1 day in the conditioning room at 21 °C and 65% RH, while the STA hair maintained its full straightness. Figure 2c shows pictures of hair after 2 days in the conditioning room. The curl formed after 1 day on the FI hair is seen to be enhanced, and further, it is accompanied by two additional distinct curls. The STA hair, however, retained most of its straightness except for the very bottom tip of the swatch after 2 days in the conditioning room. Because of their unequal lengths, the number of hairs near the bottom of the swatch are fewer and, hence, slip through the flat iron gap. As a result, the hairs at the bottom of the swatch do not receive adequate treatment as at the top and middle of the swatch. Figure 2d–f shows the pictures of hair swatches after 3, 5, and 7 days, respectively. It can be observed that FI hair became fluffed-up, showing at least three distinct curls, while only the bottom tip of STA hair showed signs of curling. Most of the top hair in the STA hair swatch maintained perfect straightness. A similar effect was observed at the end of 15 days in the conditioning room (Figure 2h). As mentioned earlier, the STA hair was well crosslinked due to the reaction of aldehyde groups from the ST solution and the amine groups from the keratin in the hair. As discussed earlier, amine groups from hair and aldehyde groups from ST react to form covalent bonds via imine (Schiff base) formation, as shown in Scheme 2 [18]. Since the crosslinked molecules are unable to move, it provides the hair significant stabilization against the humidity. The FI hair, on the other hand, is just straightened due to the mechanical force and the heat applied through flat ironing, which involves rearranging hydrogen bonds. However, the newly formed hydrogen bonds from using a flat iron (heat and mechanical treatment) are susceptible to humid conditions, and the hair reverts back to its original state over time [24]. Moisture (65% RH) present in the conditioning room is known to easily plasticize the FI hair, causing them to curl and fluff-up [25]. Four aldehyde groups present on ST significantly increase the potential for crosslinking with many amine groups present in the keratin as compared to formaldehyde or glutaraldehyde, which consist of one and two aldehyde groups, respectively. Multiple intra- and interfibrillar crosslinks formed between cortical cells, as well as within the cortex, after ST treatment allow forming a 3D network that stabilizes the hair and helps retain its desired shape. This would be true even when not all of the aldehyde groups present on ST are able to react. Commercial hair straightening products, on the other hand, contain alkali-based relaxers that break the disulfide bond in the hair. The disulfide covalent bonds provide structural integrity to the hair, and, as

a result, alkaline relaxation carried out using commercial products can weaken the hair. However, most commercial hair straightening products rely on breaking the disulfide bonds and further oxidizing or crosslinking them. A two-step process similar to that used by commercial products was used in this research to compare the effect of reduction in hair. Glutathione (GSH), commonly used to break the disulfide bonds in proteins, was used to break the disulfide bonds in keratin as the 1st step. In the second step, hair was treated with ST to crosslink the hair. The reduction step, using GSH, did not increase the hair straightening efficiency. It also did not reduce the number of passes or the temperature of the flat iron. Thus, breaking of disulfide bonds was deemed unnecessary for obtaining straightening of hair using ST, which can be a significant benefit.

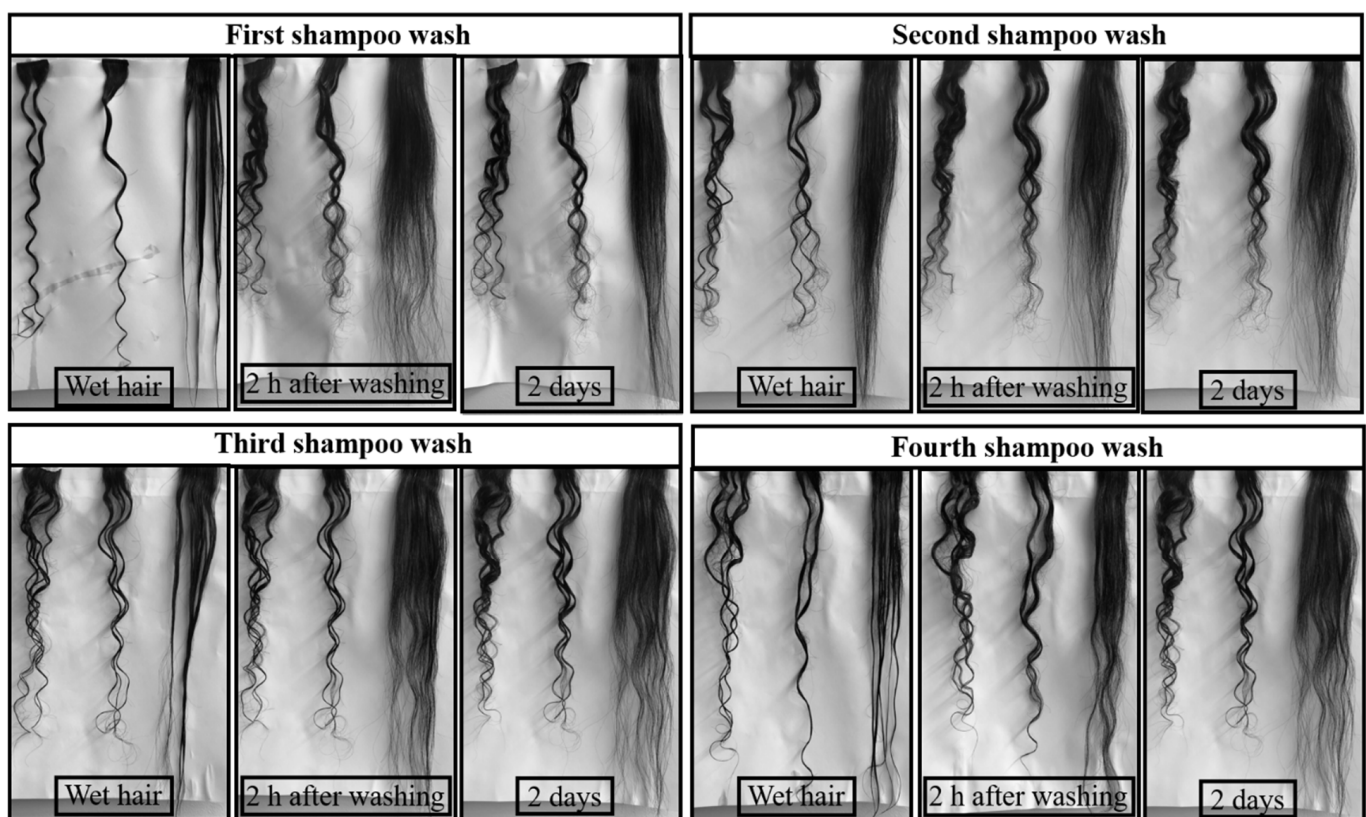


**Figure 2.** C, FI, and STA hair swatches from left to right in each picture after conditioning at (a) day 0, (b) day 1, (c) day 2, (d) day 3 (e) day 5, (f) day 7, (g) day 10, and (h) day 15.

The C, FI, and STA hair swatches were repeatedly washed using a warm 2% shampoo solution for 5 min and rinsed thoroughly under running tap water at RT until no lather was present. The wet hair swatches were placed on paper and hung on a wall in the conditioning room (21 °C and 65% RH) for 2 days before washing again. Figure 3 shows pictures of C, FI, and STA hair swatches after four shampoo washes. Pictures of wet hair were taken immediately after washing. The second set of pictures of hair swatches was taken after 2 h of drying in the conditioning room after shampoo washes and the third set after 2 days in the conditioning room. As can be seen in Figure 3, the control wet hair showed five distinct curls when washed with shampoo. Upon drying for 2 h in the conditioning room, the control hair fluffed up, causing a reduction in the length of the hair swatch and enhancing the curvature of the curls. The FI hair also curled-up immediately during the first shampoo wash, while the STA hair remained straight after the first shampoo wash. Upon drying in the conditioning room after the shampoo wash, the wet FI hair fluffed up, and the curvature of the curls increased. As a result, the length of the FI swatch was also reduced. The FI hair looked close to the C hair, as it regained all the original curls after the first shampoo



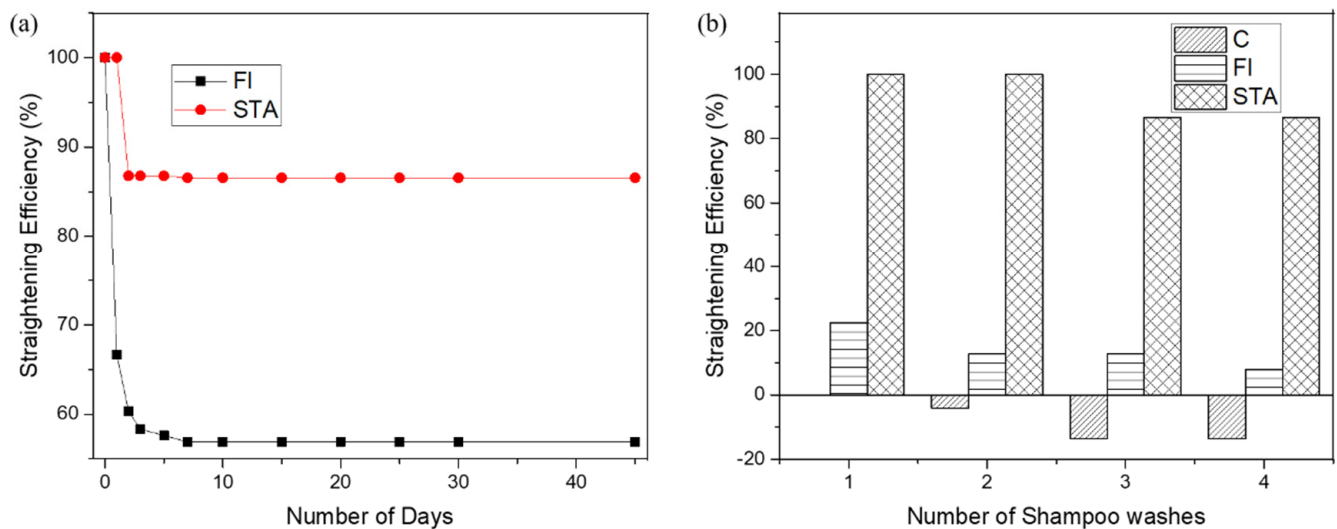
wash. As mentioned earlier, flat ironing only straightens the hair temporarily as it only involves alterations of hydrogen bonds and salt linkages [24]. As the FI hair regained most of its original curls, the length of the swatch decreased and became close to that of control hair. STA hair, however, maintained its straightness for two shampoo washes as a result of the covalent crosslinks formed, which are more permanent. As mentioned earlier, the 3D network formed within the cortex after crosslinking restricts the movement or slippage of the keratin molecules and helps retain their shape. The STA hair retained its straightness even after the third shampoo wash. It, however, started to curl around the bottom part of the swatch while drying in the conditioning room. As mentioned earlier, the bottom part of the swatch has fewer hairs that do not come in complete contact with the flat iron plates and reflect inadequate crosslinking treatment. Because of the insufficient crosslinking, the moisture in the conditioning room causes the bottom of the STA hair to begin curling. At least one curl, with low curvature, was observed after the third and fourth shampoo wash while drying with negligible reduction in the overall length of the hair swatch.



**Figure 3.** C, FI, and STA hair swatches from left to right in each picture after 4 shampoo washes.

The straightening efficiency (SE) values were calculated for FI and STA hair swatches for up to 45 days of exposure to 65% RH and for 21 °C, as well as FI and STA hair swatches after up to 4 shampoo washes, using Equation (1). Figure 4a shows the SE of FI and STA hair as a function of the days the hair swatches were hung on a wall in the conditioning room at 65% RH for up to 45 days. As seen in Figure 4a, the SE of FI and STA hair was 100% on day 0. After 1 day in the conditioning room, the SE of the FI hair reduced to 67%, while the SE of STA hair was still 100%. The change in SE was a result of at least one curl observed in the FI hair after 1 day at 65% RH, while the STA hair was fully straight (SE 100%). This can be clearly seen in Figure 2. The SE of FI hair further reduced to 60% after 2 days in the conditioning room at 65% RH as two additional curls developed on the FI swatch, while a slight curl in the bottom part of the STA hair was observed, bringing down the SE of the STA hair to 87%. The reduction in SE for FI hair to 65% was found to be statistically significant using an unpaired t-test at a significance level of 0.05. The SE

of the FI hair was further reduced to 58.3% and 57.6% as the intensity of the curvature of the curls and the number of curls increased after 3 and 5 days in the conditioning room, respectively. No additional curls, however, were observed on STA hair, and its SE remained constant at 87% for up to 5 days in the conditioning room. The SE of the FI hair further reduced to 57% after 7 days in the conditioning room and remained constant at 57% over time for up to 45 days. The SE of STA hair, on the other hand, was found to be 87% after 7 days in the conditioning room, after which it remained unchanged for up to 45 days. The change in SE of the STA hair after 2 days in the conditioning room was not found to be statistically different for up to 45 days in the conditioning room using an unpaired t-test at a significance level of 0.05. Overall, the results indicate that the SE of the STA hair was significantly higher and more permanent compared to the FI hair.



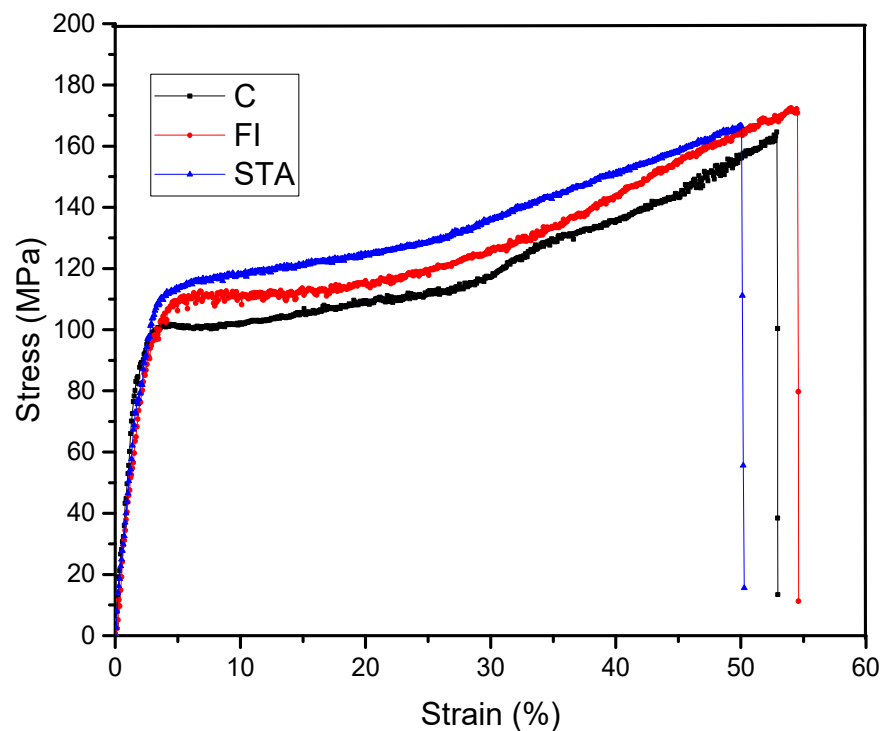
**Figure 4.** Straightening efficiency (SE) of FI and STA hair (hung vertically) at 21 °C and 65% RH as a function of (a) the number of days and (b) the number of shampoo washes.

Figure 4b shows the SE values of C, FI, and STA hair as a function of the number of shampoo washes. It should be noted that each shampoo wash was accompanied by a 2-day exposure to 65% RH at 21 °C. As can be seen from Figure 4b, the SE of FI hair reduced to 22.4% after the very first shampoo wash. This implies that FI hair regained most of its curls upon washing with shampoo. This is quite expected because flat ironing is only a temporary way of hair straightening. Hair straightening using a flat iron only involved breaking and reforming of a few hydrogen bonds in keratin, which are weak and easily disrupted by water. As a result, FI hair almost reverted back to its original curly state after washing [6]. The SE of FI hair was found to decrease further to 12.8% after the second and third shampoo washes and down to just 8% after the fourth shampoo wash. This implies that FI hair gets very close to its original state or C hair after washing with shampoo. It was also found that shampoo washing of the C hair introduces some additional curls onto the swatch, reducing their length. Thus, the SE of the C hair was negative. It was found to be −4.2% after two shampoo washes, after which it remained constant at −13.6% after the third and fourth shampoo washes. The SE of STA hair was maintained at 100% for up to two shampoo washes, after which it reduced to 87% after the third and fourth shampoo washings. Overall, the data in Figure 4b indicate that the SE of FI hair reduces significantly (very close to the control) as the hair regains most of its original curls after washing, while the SE of STA only reduces to 87% after four shampoo washes. This further confirms that the STA treatment is durable and can be used to attain permanent hair styling.

Figure 5 shows typical stress–strain plots for C, FI, and STA hair specimens. The tensile properties of C, FI, and STA individual hair specimens are summarized in Table 1. As seen in Figure 5, stress–strain plots for all hair show three distinct regions: initial Hookean region, yield region, and post-yield region [26]. The Hookean region lies between 0% and

5% tensile strain. The average tensile stress value for the C hair specimen at the end of the Hookean region was 103 MPa. In comparison, the average tensile stress values of the FI and STA hair specimens were observed to be 99.8 MPa and 99.7 MPa, respectively. These values are not significantly different compared to C hair and indicate that properties within the Hookean region remained unchanged after treatments. The tensile strains of C, FI, and STA hair specimens in the Hookean region were found to be 4.1%, 4.7%, and 4.3%, respectively. This suggests that the initial elastic characteristics of the FI and STA hair also remained unchanged after the treatments. The strain in the Hookean region comes from the extension of weaker bonds, such as hydrogen bonding within the amino acids, Van der Waals forces, and coulombic interactions [19]. Immediately following the Hookean region, the hair showed yielding behavior where a large amount of strain was associated with a very small rise in stress, signifying very low modulus or high compliance. This yield region extended from 5% to 30% strain for all hair specimens. The yielding involves the unfolding of the  $\alpha$ -keratin to  $\beta$ -keratin conformation, which allows a larger deformation in the hair before breaking [19,26]. Strain-hardening phenomenon was observed beyond the yield region for all fibers [19,26]. The strain-hardening region extends from 30% to 50% strain and ends when the hair ruptures. The breaking or ultimate fracture stress values for C, FI, and STA hair specimens were found to be 164 MPa, 171 MPa, and 166 MPa, respectively. The differences in these fracture stress values were found to be statistically insignificant, using an unpaired t-test, at a significance level of 0.05. This implies that the tensile stress of the hair strands was unaffected after flat ironing performed in this study, as well as the sucrose ST. It is known that the keratin in hair is susceptible to thermal degradation during flat ironing, which results in the weakening of the hair strands [6]. Continual heat treatments, such as flat ironing, particularly in wet conditions, increase hair damage [27]. In the present study, flat ironing of hair in a wet state was intentionally avoided, and ST solution was allowed to dry before flat ironing of hair. While the pH of most commercial hair straightening products is highly alkaline (above 10), the pH of sucrose ST was adjusted to neutral pH of 7 to avoid alkaline denaturation of keratin protein and retain tensile properties. Overall, the tensile results suggest that the tensile properties of hair remain unchanged after the ST treatment and, hence, could be a viable, healthy alternative to currently used toxic hair crosslinkers. It is also clear from the data presented in Table 1 that the FI treatment reduced the initial modulus (Young's modulus) to 2.3 GPa from 2.6 GPa obtained for C hair. However, after the ST treatment, the modulus recovered back to 2.6 GPa, as a result of crosslinking. The crosslinked network formed by ST, however, does not seem too highly crosslinked, and overall, the ST treatment results in the least damage to hair.

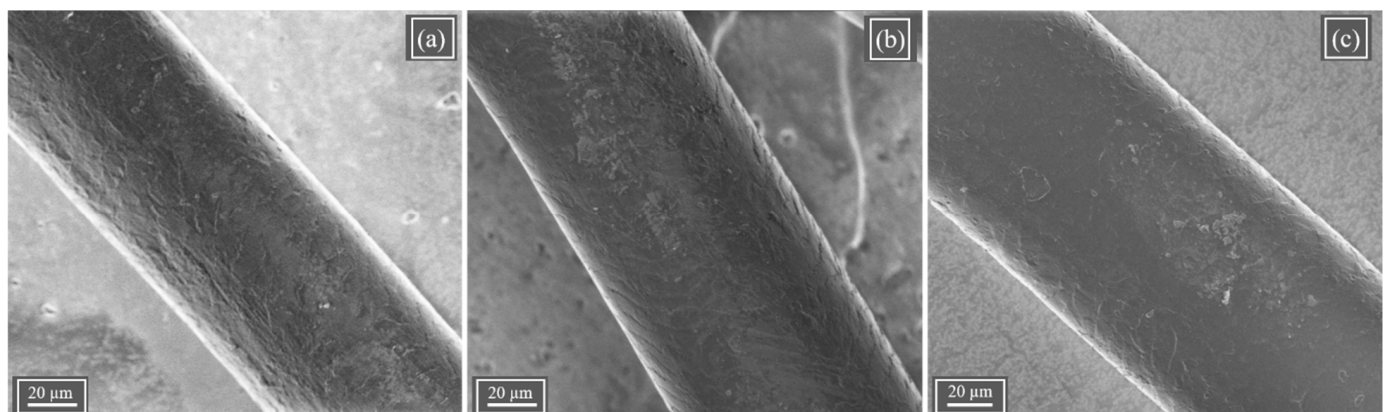
Figure 6 shows typical SEM images of C, FI, and STA hair specimens. As seen in Figure 6a, the control hair showed typical scales on the surface. No visible change or damage to the scales on the surface was observed after FI or STA treatments on the hair. Since the excess heat of the flat iron can damage the hair, especially the surface scales, which are in contact with the flat iron, if carried out in the wet condition, care was taken to ensure that the hair was dry after treating with STA (by leaving them to air dry at RT for 10 min) before flat ironing. Most of the keratin crosslinking by ST solution occurs inside the hair as it is a small molecule and can penetrate the hair easily, leaving the surface of the hair undamaged after STA treatment.



**Figure 5.** Typical stress–strain plots for C, FI, and STA hair.

**Table 1.** Tensile properties of the C, FI, and STA hair.

Hair Type	Diameter ( $\mu\text{m}$ )	Initial Hookean Region			Post Yield Region	
		Stress (MPa)	Strain (%)	Young's Modulus (GPa)	Stress (MPa)	Strain (%)
C	$68.2 \pm 11.9$	$103 \pm 36.9$	$4.1 \pm 0.6$	$2.6 \pm 1.1$	$163.8 \pm 54.8$	$49.3 \pm 7.5$
FI	$73.3 \pm 07.9$	$99.8 \pm 34.3$	$4.7 \pm 1.1$	$2.3 \pm 1.0$	$171.0 \pm 35.6$	$51.8 \pm 8.6$
STA	$74.0 \pm 16.0$	$99.7 \pm 28.1$	$4.3 \pm 1.4$	$2.6 \pm 1.2$	$166.1 \pm 44.0$	$49.7 \pm 5.8$



**Figure 6.** SEM images of (a) C, (b) FI, and (c) STA hair.

## 5. Conclusions

The present study has successfully demonstrated that hair can be crosslinked and stabilized using a ‘green’ sucrose-based crosslinker. Sucrose was oxidized using  $\text{NaIO}_4$  to convert the secondary hydroxyl groups to aldehyde groups, thus producing sucrose tetraaldehyde. The crosslinking of hair was accomplished by allowing sucrose tetraalde-



hyde to diffuse inside the hair cortex prior to flat ironing of hair. The chemical crosslinking via covalent bond formation (imine) from the reaction between amine groups in keratin and aldehyde groups in sucrose tetraaldehyde resulted in a stable crosslinked 3D network within the hair cortex. The hair straightening process was optimized to achieve maximum straightening efficiency with the least damage to the tensile properties or the surface scales of the hair. The straightening was found to be stable for up to 4 shampoo washings. These promising results show a novel ‘green’ and innovative alternative of chemical treatment for hair styling without being exposed to currently used toxic and carcinogenic chemicals. The process developed here can be easily used for any natural hair and animal hair, including dog and wool.

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