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# Pollution Damage and Protection of Asian Hair

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**Abstract:** Cigarette smoke was used to simulate a polluted environment and an experiment was performed to reveal how virgin and bleached hair are damaged by a polluted environment. The dry/wet combability, surface contact angle, tryptophan content, and cuticle morphology of the smoke exposed hair were evaluated, and compared to unexposed virgin hair. The results showed that pollution exposure can cause significant chemical damage to hair. In particular, virgin hair exposure to pollution can cause damage to the hair cuticles (higher wet/dry combing), protein degradation, and a more hydrophilic hair surface. The experiment also demonstrated that the styling polymer, polyimide-1 (isobutylene/dimethyl amino propyl maleimide/ethoxylated maleimide/maleic acid copolymer), can provide effective protection against such hair damage.

**Keywords:** hair damage; cigarette smoke; pollution; protein damage; polyimide-1

## 1. Background

Personal care products around the world claim to deliver a wide variety of benefits—in particular, the prevention and repair of damage caused by external stress [1]. The most common external stress to hair includes not only mechanical/chemical damage, UV exposure, and heat treatment, but also exposure to air pollution. Research on hair care products and ingredients offering protection against air pollution has become a hot topic [1–3]. In 2016, Mintel conducted a survey of consumers of hair care products aged from 20 to 49 years, in which 41% of respondents expressed their concern about hair damage by air pollution. There are many air pollutants, including polycyclic aromatic hydrocarbons (PAHs), volatile organic compounds (VOCs), oxides, particulate matter (PM 2.5/10), and ozone. The level of PM 2.5/10, a complex mixture of organic/inorganic solid and liquid pollutants, is a key indicator for measuring and monitoring air pollution [4,5]. The particle size of PM 2.5 is only 1/30 of the diameter of human hair. Its adsorption on hair not only reduces glossiness and moisture, but also causes chemical damage through attached toxic and oxidizing pollutants penetrating inside the hair [5]. Long-term exposure to air pollution can cause damage to both the hair and scalp [1,3,4,6]. There are four methods to protect hair from air pollution: (1) perform deep cleaning to completely remove pollutants from the hair and scalp; (2) reduce air pollution sources, resulting in less solid particulate pollutants becoming adsorbed into hair; (3) provide effective protection for hair to prevent pollutants from entering the hair and causing damage; and (4) neutralize pollutants or the effect by pollutants.

In previous published work, especially in studies related to skin protection and skin care, researchers have often used carbon powder or cigarette smoke to simulate a polluted environment [5,7]. With regard to hair care, some studies use standard dusts to observe the physical adsorption of PM 2.5/10 into hair and its effect on the physical properties of hair, such as glossiness and combability [8,9]. However, those studies only revealed the anti-dust properties, instead of anti-pollution properties. By using cigarette smoke in a closed chamber to simulate a polluted environment with a high concentration of PM 2.5/10, we designed an accelerated experiment to study the damage to both virgin and bleached Asian hair tresses from exposure to air pollutants. Various parameters, such as cuticle morphology, surface contact angle, and tryptophan content, as well as wet/dry combing changes, were evaluated. Polyimide-1, an isobutylene/dimethyl aminopropyl maleimide/ethoxylated maleimide/maleic acid copolymer, is a unique styling polymer with a long hydrophobic side, and binds tightly on the hair protein structure for complete hair coverage (Figure 1). It is a water soluble polymer with excellent styling and hair volumizing properties. The application of polyimide-1 as a styling polymer was evaluated for its ability to provide hair with effective protection against such air pollutants.

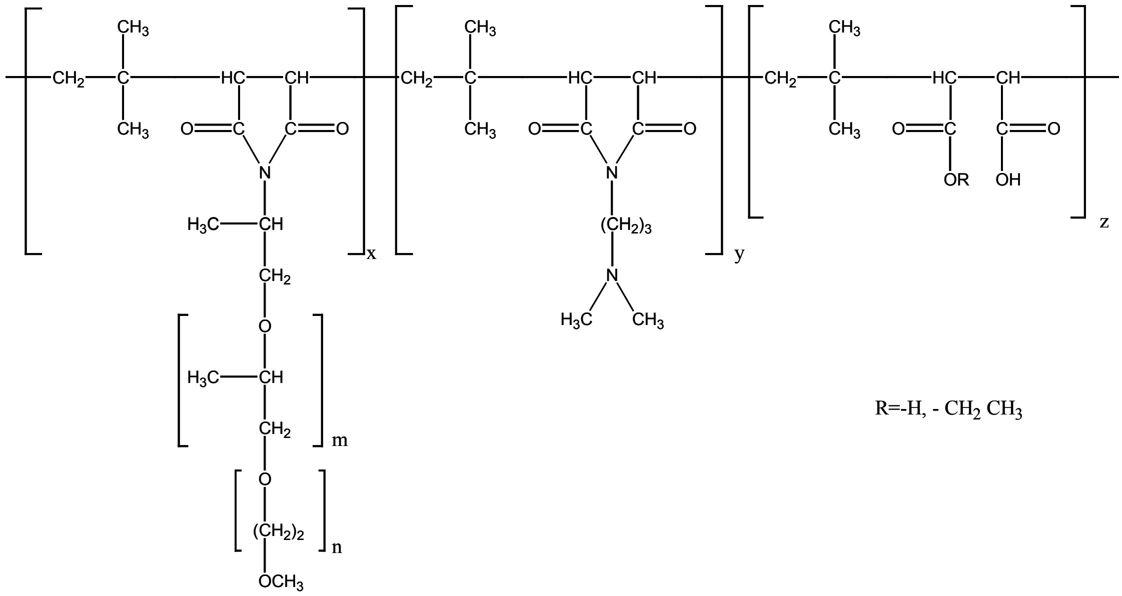



**Figure 1.** Chemical structure of polyimide-1.

## 2. Experiments

### *2.1. Materials and Instruments*

The following materials and instruments were used to conduct these studies: virgin and bleached Asian hair (International Hair Importers & Products, Glendale, NY, USA); Hong Mei cigarettes (Yuxi Cigarette Factory, Yunan, China); sodium laureth sulfate ($w$ = 70%, Shanghai Aowei Chemical Co., Ltd., Shanghai, China); methanol, dichloromethane, and AR (Sinopharm Chemical Reagent Co., Ltd., Beijing, China); polyimide-1 (Trade name: Aquaflex XL-30, Ashland, Carvington, KT, USA); Instron 4592 tensile tester (Instron, Norwood, MA, USA); Fluoromax-4 fluorescence spectrophotometer (HORIBA, Kyoto, Japan); a contact angle tester (Shanghai Solon Information Technology, Shanghai, China); scanning electron microscopes Sirion 200 (SEM) (Oxford Instruments, Abingdon, UK); and an air pollution simulation chamber (Shanghai Lijie Scientific Instruments).

### *2.2. Experimental Methods*

#### 2.2.1. Cigarette Smoke Chamber

Cigarette smoke from a smoke generator was channeled into a closed chamber by a pump to simulate an ambient environment containing significant amounts of airborne pollutants. Cigarette smoke mainly contains carbon monoxide, PM 2.5/10, nicotine, nitrogen oxides, and tar, etc. PM 2.5/10 accounts for a large portion of the particulate matter and usually has nitrogen oxides, sulfides, and heavy metals absorbed into its surface. Cigarette smoke is therefore similar to air pollution in terms of the pollutants it contains [5,7,10].

2.2.2. Hair Exposure Process

Virgin and bleached hair tresses were cleaned with a 5% SLES solution, then sequentially immersed in a graduated cylinder containing methanol, dichloromethane, and water for 20 min, to remove extra dirt and grease, and finally were hung up to be air-dried. The dry/wet combing, surface contact angle, tryptophan level, and cuticle morphology of the tresses [11] were measured. The tresses were exposed to a smoke chamber for one hour with a smoke concentration of six cigarettes/42 L, PM 2.5 at 1000 ppm consistently, then cleaned with the same method used in the pre-treatment stage to remove residue, and finally hung up to be air-dried. This procedure was repeated for six cycles in total. The control samples were cleaned with the same method used at the pre-treatment stage and this was repeated for six cycles. The parameters were measured again for comparison to the initial data. For polyimide-1 protected samples, 0.9% polyimide-1 (active dosage) aqueous solution was evenly applied by spraying on hair tress. The solution was sprayed at three fixed positions corresponding to the tip, middle, and root of hair tress. One spray was made for each position, and the tress was then turned around and sprayed again in the same way.

2.2.3. Hair Damage Evaluation

The dry/wet combing was measured by combing work, which is defined as the work carried out by a comb going through the hair (Instron). The combing work was calculated by averaging the values of six measurements. Surface hydrophobicity was measured by the contact angle of a water droplet on a flat surface of hair tress fixed by a stand [11]. The tryptophan content was measured directly on the hair tress with a fluorescence spectrophotometer. The normalized tryptophan fluorescence intensity was calculated by taking an average of different sections of a hair tress, where a higher average indicates a higher tryptophan content [12]. The cuticle morphology was observed with a scanning electron microscope at 1000× magnification.

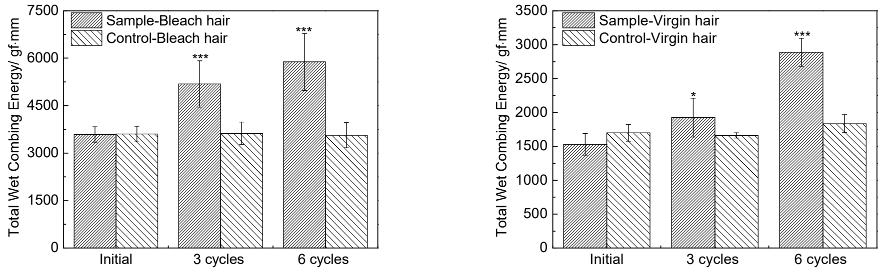
### *2.3. Statistical Analysis*

Three parallel hair tresses were measured for each sample. Each hair tress was measured three to five times for statistical analysis. The JMP 10.0.1 software for statistical analysis (oneway ANOVA T test) was used and the relevant charts show data values in the form of "average ± standard deviation".

## 3. Results and Discussion

### *3.1. Wet Combing*

As a major indicator of hair health condition, wet combing shows the friction between the comb teeth and the hair, as well as among hair fibers, which is affected by damage to the hair cuticle and protein [11]. More damage will make hair more hydrophilic, leading to more tangled wet hair and a higher wet combing force. Therefore, undamaged or healthy hair has the lowest wet combing force [13]. As shown in Figure 2, the wet combing work of the control sample after the third and sixth cycles were basically the same as the initial sample after pre-treatment, which indicates that surfactants and solvents do not damage the hair and increase wet combing work. After exposure to smoke, both virgin and bleached hair require significantly higher wet combing work. In particular, the combing work of virgin hair after six cycles was nearly twice the initial value after pre-treatment, which is close to the initial wet combing work of the bleached hair. It can be concluded that air pollution can cause irreversible chemical damage to hair, especially virgin hair.

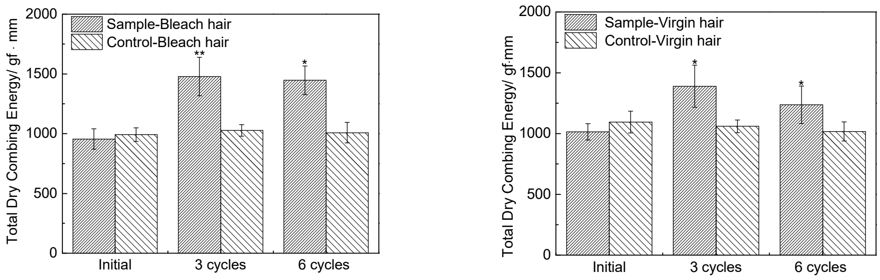



(**a**) (**b**)

**Figure 2.** The wet combability of (**a**) bleach hair and (**b**) virgin hair sample (exposed) and control (unexposed, washed by solvents) groups after pre-treatment, and the third and sixth cycles treatment. Note: comparison to the control group, * $p < 0.05$, *** $p < 0.001$.

### 3.2. Dry Combing

When particulate matter (PM 2.5/10) and toxic pollutants are absorbed into the hair surface, the dry combing force will increase [14], while the absorption of oils, such as tar, which are commonly present with PM 2.5/10, will decrease the combing force. Hair exposed to cigarette smoke has a lower dry combing work value than the control sample. Therefore, combing force cannot be used as an indicator for hair damage before cleaning by surfactants and solvents. This is why a serial cleaning process was performed to remove the residue caused by the smoke and allow the real hair damage to be evaluated, rather than an anti-dust evaluation. As shown in Figure 3, the dry combing work for the control samples after the third and sixth cycles were basically the same as the initial values, while exposed samples after three cycles showed increases in the initial dry combing work of 40–50%. The values did not increase after the sixth cycle of smoke exposure, indicating that the hair damage reached the maximum level even after three cycles of smoke exposure. Both hair cuticle and protein damage will have adverse effects on dry combing. In particular, raised cuticles will cause an uneven hair surface, leading to increased friction between the comb and hairs [3,13].

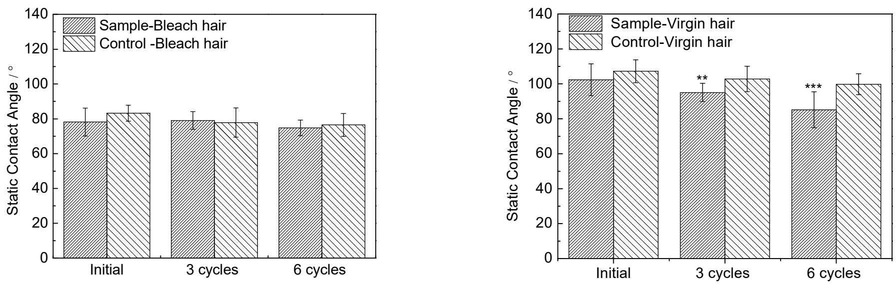



(**a**) (**b**)

**Figure 3.** Dry combability of (**a**) bleach hair and (**b**) virgin hair sample (exposed) and control (unexposed, washed by solvents) groups after pre-treatment, and the third and sixth cycles treatments. Note: comparison to the control group, * $p < 0.05$, ** $p < 0.01$.

### 3.3. Contact Angle

The outermost layer of hair is composed of a hydrophobic 18-methyl eicosanoic acid (18-MEA) lipid, which is most vulnerable to external damage. Without the natural protection of 18-MEA, the hair will be more hydrophilic and its cuticle and inner structure will be more easily damaged, due to direct exposure to external factors such as air pollution. 18-MEA is connected to keratin in the same layer through thioester bonds, which can be damaged by alkaline ingredients in air pollution, such as ammoniac compounds, leading to loss of the 18-MEA layer. The contact angle between a water drop and the hair surface can be measured to determine to what extent 18-MEA has been lost [3,11]. Figure 4 shows the hydrophilicity of the exposed and control samples after several cycles of smoke exposure. The contact angles of the bleached hair in both the exposed and control groups did not differ significantly with the initial contact angle after pre-treatment. According to our analysis, this is because most of the 18-MEA was lost due to the hair bleaching process [13]. But the contact angle of the virgin hair gradually decreased throughout the experiment. The contact angle after six exposure cycles was about 85% of the initial contact angle after pre-treatment, close to the initial contact angle of the bleached hair.




(**a**) (**b**)

**Figure 4.** The hydrophilic properties of (**a**) bleach hair and (**b**) virgin hair sample (exposed) and control (unexposed, washed by solvents) after pre-treatment, and the third and sixth treatments. Note: comparison to the control group, * $p < 0.01$, *** $p < 0.001$.

### 3.4. Hair Protein Level

Protein is the key structural component of hair, and can be degraded through exposure to heat, UV, and oxidizing stress. Hair protein level can be used as an indicator of the hair damage level [7]. There are various methods by which to measure protein degradation, such as Dynamic Stability Control (DSC), Fourier Transform infrared spectroscopy (FTIR), etc. In this study, a fluorescence spectrophotometer (Fluoromax-4, HORIBA, Kyoto, Japan) was used to measure the tryptophan level present in the hair, with the excitation wavelength set to 290 nm. Tryptophan is one of the amino acids that can be found in keratin, and has a unique emission wavelength of 335 nm, making it a natural indicator for measuring protein degradation in hair. The more severe the damage is, the lower the presence of tryptophan in the hair [12]. By comparing the tryptophan content before and after hair treatments such as perming, coloring, and straightening, the hair damage from such treatments can be measured. As shown in Table 1, the tryptophan content of the bleached hair in the experimental group did not decrease after several exposures to cigarette smoke. This is because about 50% of the tryptophan had already been lost due to hair bleaching by highly oxidizing and alkaline solutions, so most of the tryptophan in the surface and middle layers of the bleached hair had been degraded already [12]. In contrast, the tryptophan content of the virgin hair after smoke exposure gradually decreased throughout the experiment. The tryptophan content after six exposure cycles was about 90% of the initial tryptophan content after pre-treatment.

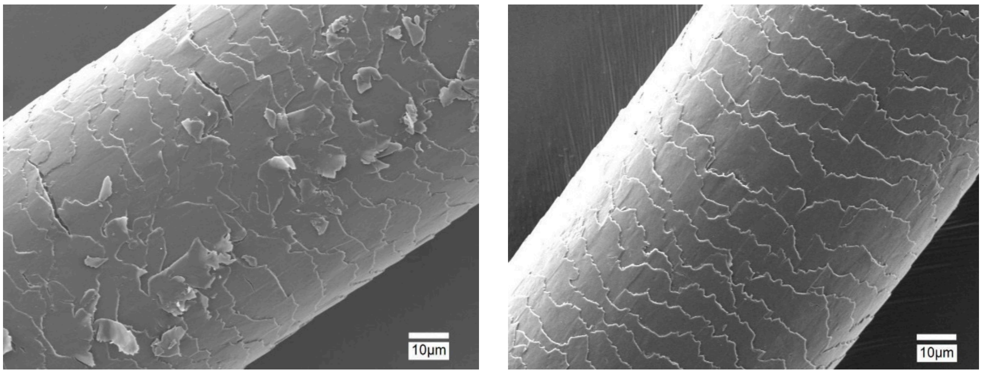
**Table 1.** Percentage change of the tryptophan content of the experimental and control groups after the third and sixth treatments.

| Number of Exposures | Percentage Change of Tryptophan Content (%) | | | |
|---|---|---|---|---|
| | Exposed Hair (Bleached) | Control Hair (Bleached) | Exposed Hair (Virgin) | Control Hair (Virgin) |
| 3 | 0.23% ± 0.010 | 1.41% ± 0.005 | −3.98% ± 0.010 ** | −0.38% ± 0.007 |
| 6 | −0.66% ± 0.009 | 1.20% ± 0.002 | −8.72% ± 0.016 ** | 0.49% ± 0.017 |

Note: comparison to the control group, ** $p < 0.01$.

### 3.5. Cuticle Morphology

With the loss of the 18-MEA layer, hair cuticles lose protection, leading to direct exposure to stresses such as air pollutants, which can cause keratin breakdown. The hair cuticles will therefore become raised and shredded instead of smooth and intact, with less hair glossiness, moisture, etc. [7] Figure 5 shows the cuticle morphology of unexposed virgin hair and virgin hair after six exposure cycles. The cuticles of the polluted hair in the experimental group are severely shredded and raised, while those of the control sample are smooth and intact. This illustrates the severe damage that air pollution exposure can cause to the outermost layer of hair cuticles. It is worth noting that there is no difference in cuticle morphology between bleached hair before and after smoke exposure, since the cuticles have already been damaged by the bleaching process (data not shown).




(**a**) (**b**)

**Figure 5.** Cuticle morphology of (**a**) unprotected virgin hair after six exposure cycles and (**b**) unexposed virgin hair.

### 3.6. Proposed Mechanism

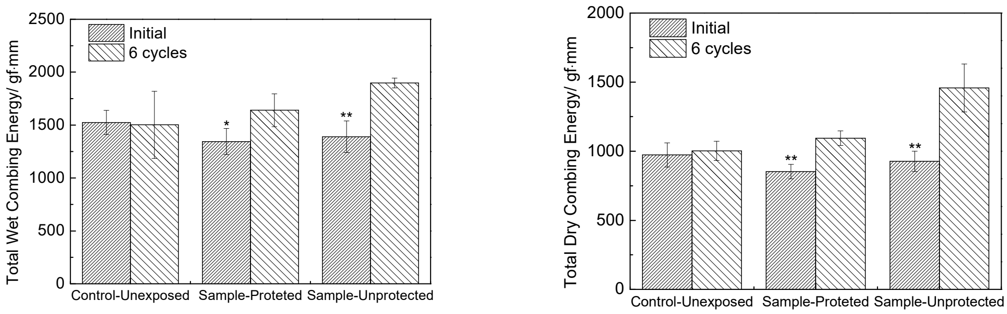
Similar to air pollution, cigarette smoke also contains three formats of pollutants: toxic gases (carbon monoxide, formaldehyde, nitrogen oxides etc.); liquid droplets (tar, nicotine etc.); and solid particulate matter (ashes, heavy metals, arcinogenic PAHs, sulfides etc. absorbed on surface). It contains all important classes of pollutants that are 150 times higher than air pollution, but this could be handled in the lab with minimal influence on operators. Among these three formats of pollutants, toxic gases could easily penetrate inside hair fibers with minimal adhesion. Liquid droplets (oil) will exhibit the most adhesion due to the hydrophobic surface of hair, and penetrate inside hair fibers to a certain distance. A certain number of solid particles also adhere on the hair surface, and the attached toxic and oxidizing pollutants will penetrate inside the hair fibers when the pollutants were dissolved in liquid droplets (oil) or water (humidity).

Based on the above observations, it could be proposed that the proteins inside hair were mostly oxidized by toxic gases and tar, while the wet/dry combing, cuticle morphology changes were influenced by all pollutants which oxidized 18-MEA layers and cuticles, resulting in a hydrophilic hair surface. It is worth noting that cigarette smoke exposure should be considered as an accelerated experiment to study the damage to both virgin and bleached Asian hair tresses from exposure to air pollutants, since normal air pollutions will not contain such a high amount of toxic gases and liquids. By this accelerated method, several styling polymers, including polyvinyl pyrrolidone (PVP), PVP/VA copolymer, and polyimide-1, etc., were screened for the anti-pollution benefit. Polyimide-1 gave the best performance, while other styling polymers did not give effective protection against such air pollutants (data not shown).

### 3.7. Polyimide-1 for Anti-pollution Treatment

As shown in the above data, air pollutants, as simulated in these studies by cigarette smoke, can physically adhere to hair. Most importantly, these pollutants can cause irreversible chemical damage to the hair protein and cuticle, leading to more hydrophilic hair, and worse hair conditioning in terms of virgin hair. The pollutants absorbed into the hair surface can be removed through immediate cleaning, but the chemicals that penetrate inside the hair cannot be removed, and will therefore accumulate, causing long-term damage. Therefore, the most effective solution to protect hair from the effects of exposure to air pollution would be one that prevents any direct contact between hair and air pollutants that can penetrate inside the hair. A polymer film could form a continuous protective layer on the hair surface, and provide effective protection against such airborne pollutants. However, it is important to select polymers with a unique structure, e.g., with an affinity for hair rather than pollutants, to provide both a certain styling benefit and protection against air pollution exposure. Various polymers have been studied, with results showing that polyimide-1 can provide the most effective protection against exposure to cigarette smoke (data not showed). In this study, aqueous polyimide-1 solution was sprayed on virgin hair before exposure to smoke as described in the experiments section, and the results are discussed below.

Figure 6 shows the wet and dry combing of the protected and unprotected hair after several smoke exposures. The wet combing work of the unprotected hair after six exposure cycles increased by 45% after pre-treatment, while that of the hair protected by polyimide-1 increased by only 20%. The dry combing work showed the same trend.




(**a**) (**b**)

**Figure 6.** (**a**) Wet and (**b**) dry work combing of the protected and unprotected hair, with pre-treatment and after six cycles of smoke exposure. Note: comparison to pre-treatment, * $p < 0.05$, ** $p < 0.01$.

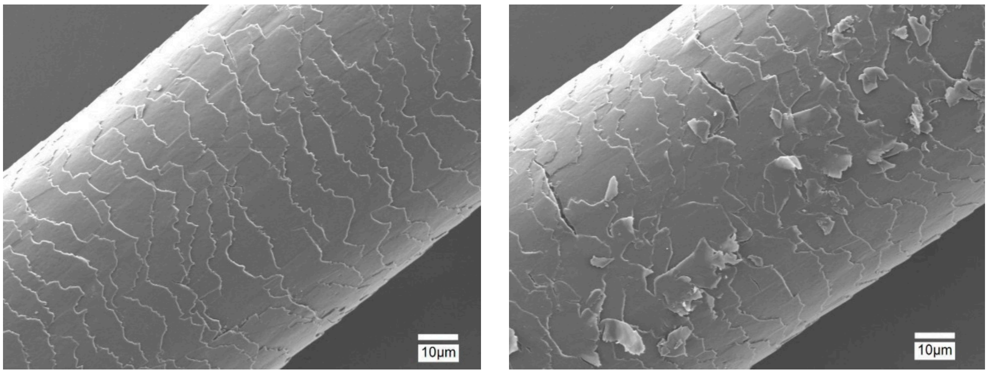
Table 2 shows the percentage decrease of the contact angle and the tryptophan content of the protected and unprotected hair after six cycles of smoke exposure. The contact angle of the control sample decreased slightly due to the cleaning by solvents of the oils and fats inside the hair. There was also a small decrease for the polyimide-1-protected hair, but this result was much better than for the unprotected hair. The percentage change of the tryptophan content showed the same trend as the contact angle. The tryptophan content of the control group was basically the same as the initial content. For the hair protected by polyimide-1, there was a slight decrease in tryptophan content, but for the unprotected hair, it was about 90% of the initial value. Polyimidie-1 does not interfere with the fluorescence measurements used for the quantification of tryptophan content, especially after solvents wash. Most of polyimide-1 was washed off by the solvents.

As shown in Figure 7, the cuticle morphology observed with the scanning electron microscope provided more visible proof of the ability of polyimide-1 to provide virgin hair with effective protection against exposure to cigarette smoke. The cuticle of the unprotected hair in the experimental group was raised, shredded, and severely damaged, but the cuticle of the hair protected by polyimide-1 was relatively intact and smooth. This means the combing work and contact angle of the protected hair are basically the same as their initial values.

**Table 2.** Percentage change of the contact angle and tryptophan content of the protected and unprotected virgin hair in the experimental group after the sixth treatment.

| Parameter | Percentage Change (%) | | |
|---|---|---|---|
| | **Control Hair (Unexposed)** | **Protected Hair (Exposed)** | **Unprotected Hair (Exposed)** |
| Contact Angle | −2.83% ± 0.007a | −3.29% ± 0.003a | −10.38% ± 0.004b |
| Tryptophan | −0.07% ± 0.001a | −1.28% ± 0.007a | −8.26% ± 0.013b |

Note: for a specific tested parameter, the data values marked by the same letter indicate an insignificant difference ($p < 0.05$).




(**a**) (**b**)

**Figure 7.** Cuticle morphology of the (**a**) protected and (**b**) unprotected virgin hair after six exposure cycles.

## 4. Conclusions

This study designed an accelerated experiment on the changes in hair properties, such as combability, contact angle, tryptophan content, and cuticle morphology, in an environment containing a high concentration of airborne pollutants such as PM 2.5/10, as simulated by cigarette smoke in a closed chamber. The air pollutants absorbed into hair not only show temporary physical adhesion, but also cause irreversible chemical damage. Though immediate cleaning can reduce the level of physical damage caused to hair, the harmful compounds in air pollutants can penetrate inside the hair and accumulate, causing damage to the hair cuticle and protein breakdown. The method used in this study can act as a reference point for further research on how and to what extent hair can be damaged by exposure to air pollution. This experiment further revealed that polyimide-1, with its unique film-forming properties, when applied as a styling polymer, can provide a protective film for hair, to help prevent the hair cuticles and protein from being damaged by exposure to certain types of airborne pollutants. The consumer perception of polyimide-1 in final products for pollution protection need to be investigated further.

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**Author Contributions:** Xin Qu and Bert Kroon conceived and designed the experiments; Bernice Niu and Xin Qu performed the experiments, analyzed the data, and wrote the paper; and Linda Foltis supervised the study. All authors read and approved the final manuscript.

**Conflicts of Interest:** The authors declare no conflict of interest.

## References


1. Emmanuelle, M. *Protection-Shielding against the Impact of Pollution, Stress and UV*; In-Cosmetics Asia: Bangkok, Thailand, 2014.
2. Li, S.; Liu, H. The aging and anti-aging of hair. *Deterg. Cosmet.* **2010**, *33*, 24–27.
3. Takada, K.; Nakam, A.; Mastsuo, N.; Nishida, Y.; Hayashi, T. Influence of oxidative and/or reductive treatment on human hair: Analysis of hair damage after oxidative and/or reductive treatment. *J. Oleo Sci.* **2003**, *52*, 541–548. [CrossRef]
4. Rohde, R.A.; Muller, R.A. Air pollution in China: Mapping of concentrations and sources. *PLoS ONE* **2015**, *10*, 1–18. [CrossRef] [PubMed]
5. Blosl, N.; Ott, R.; Schacht, K. Efficient hair protection—The multi-functional silk polypeptides new and promising strategy against pollution. *SOFW J.* **2017**, *143*, 43–45.
6. Isabelle, A. Method of Using Fibers as an Antipollution Agent in a Cosmetic Composition. U.S. Patent 20020031533, 14 March 2002.
7. Adamson, J.; Azzopardi, D.; Errington, G.; Dickens, C.; McAughey, J.; Gaça, M.D. Assessment of an in vitro whole cigarette smoke exposure system: The Borgwaldt RM20S 8-syringe smoking machine. *Chem. Central J.* **2011**, *5*. [CrossRef] [PubMed]
8. Chang, X.W.; Cox, B.; Thomas Föster, T. Study of the dust deposition prevention effect of hair shampoo and conditioner formulations containing moringa oleifera seed extract. In Proceedings of the 23nd IFSCC Conference, Zurich, Switzerland, 21–23 September 2015.
9. Pham, D.M.; Boussouira, B.; Moyal, D.; Nguyen, Q.L. Oxidization of squalene: A human skin lipid: A new and reliable marker of environmental pollution studies. *Int. J. Cosmet. Sci.* **2015**, *37*, 357–365. [CrossRef] [PubMed]
10. Wang, B.; Hang Ho, S.S.; Ho, K.F.; Huang, Y.; Chan, C.S.; Feng, N.S.Y.; Simon, H.S.I. An environmental chamber study of the characteristics of air pollutants released from environmental tobacco smoke. *Aerosol Air Q. Res.* **2012**, *12*, 1269–1281. [CrossRef]
11. Ito, H.; Muraoka, Y.; Höcker, H. Damage of hair fibers as evaluated by an electrical capacitance technique. *J. Soc. Cosmet. Chem.* **1994**, *45*, 183–192.
12. Jachowicz, J.; Mcmullen, R.L. Tryptophan fluorescence in hair—Examination of contributing factors. *J. Cosmet. Sci.* **2011**, *62*, 291–304. [PubMed]
13. Velasco, M.V.R.; Dias, T.C.S.; Freitas, A.Z.; Vieira Júnior, N.D.; de Oliveira Pinto, C.A.S.; Kaneko, T.M.; Baby, A.R. Hair fiber characteristics and methods to evaluate hair physical and mechanical properties. *Br. J. Pharm. Sci.* **2009**, *45*, 153–164. [CrossRef]
14. Wire, S.L.; Riley, R.G.; Rutherford, K.L.; Birtwistle D.H. Hair Treatment Compositions Containing Particulate Matter. CN 1413102, 23 April 2003.