The Effects of Cationic/hydrophobic-modified Hydroxyethyl Cellulose Polymers on Heat-Styling Damage

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Abstract (Maximum of 250 words)

Cationic/hydrophobic-modified hydroxyethyl cellulose (cat-hmHEC) polymers exhibit a variety of unique characteristics that strongly distinguish them from other cationic polymers. Previous studies showed that cat-hmHEC polymer can be used as an alternative for silicone in conditioner applications. The hydrophobic chain contributes to softness and smoothness while the cationic moiety increases the polymer deposition onto the surface of the hair fiber. In this study, cat-hmHEC polymer was evaluated as a thermal protectant and applied to the hair in a leave-in format. The hair tresses were treated using a flat iron, and the keratin denaturation and thermal properties of the polymer-treated hair fibers were analyzed using differential scanning calorimetry (DSC). Surface properties of hair were evaluated using scanning electron microscopy (SEM). To better understand the thermal protection mechanism, the polymer was compared to different variations of cellulosic polymer, including hydroxyethyl cellulose (HEC) and polyquaternium-10 (PQ-10) polymer. The polymer pretreatment significantly increases the denaturation temperature, T_d, and denaturation enthalpy (ΔH) in comparison to the thermally treated hair without a protectant. Among all the polymers that were screened, cat-hmHEC polymer provided the highest level of thermal protection, while HEC and PQ-10 polymers provided the lowest level of protection at the same use level (1 w/w %). Results suggested that hydrophobicity plays a crucial role in reducing hair damage upon exposure to heat.

Keywords: cationic polymers; cellulose; hair; hmHEC polymers; heat protection.

Introduction.

Hair straighteners or curling irons have commonly been used to create temporary hair styles. after heat treatment hair typically feels soft with improved alignment and less frizz [1, 2]. While thermal treatment provides numerous benefits, it can lead to hair damage which has become a major concern in hair health. The heating devices can generate temperatures higher than 200 °C, which is sufficient to cause both physical and thermal damage to the hair fiber. During the thermal treatment, the moisture in the hair is removed, leading to hydrogen bonding rearrangements and a temporary change in the hair structure and style [3]. Such rearrangements can be disrupted in the presence of water, i.e. washing or high humidity, and the hair can resume its natural shape. Recent studies show excessive heat (between 150-250 °C) can cause the disulfide bonds to break [4], and heat treatments between 130-164 °C can result in a change in the hair's mechanical properties [5] and a decomposition of chromophores, specifically tryptophan and the oxidized products of tryptophan [6]. Consumers also have an understanding of the negative impact and are looking for products that can protect their hair from thermal damage.

There are many types of materials that offer heat protection benefits. Most of them are able to form a film-like structure on the surface of the hair fiber, preventing excessive water loss caused by the heat treatment and slowing down the transfer of heat to the hair [3]. In 1998, 1 w/w % of polyvinylpyrrolidone/dimethylaminopropylamine (PVP/DMAPA) acrylates copolymer, polyquaternium-70, or hydrolyzed wheat protein was found to help suppress hair damage by 10-20% when used as leave-in treatments [7]. Silicones have also been used to protect the hair from heat damage due to their low thermal conductivity and film forming ability [8-11]. These ingredients are normally formulated as a leave-in oil, cream or spray and applied to hair prior to heat application.

In the past few years, consumer awareness of their health and wellbeing has shifted industrial focus towards more biobased and natural products. Despite their desire for these materials, most consumers will not sacrifice product performance and efficacy. This has become a challenge for the beauty care industry to identify new natural ingredients that address consumers' needs while still maintaining high performance. In response to growing demand for natural alternatives, Dow has developed cat-hmHEC polymers for use in hair care applications to provide desirable sensorial attributes to the consumer. Previous studies showed that cat-hmHEC polymers exhibit a broad range of benefits through numerous product formats such as shampoos and conditioners [12]. In this study, the benefits of cat-hmHEC polymer were further extended to thermal protection in a leave-in format. The effect of the polymer pretreatment on the thermal denaturation of keratin was investigated. Differential scanning calorimetry (DSC) was used to analyze the denaturation of keratin and the temperature at which it occurs in the hair fibers.

Materials and Methods.

Most polymers used in this study were received from Dow unless specified otherwise. For the diphenylamine assay, all reagents were purchased from Sigma Aldrich or Fisher Scientific and used as received. Throughout this study, medium brown virgin hair was used for the treatment and evaluation unless specified otherwise.

Table 1. General characteristics of the polymers used in this study

Polymer name	Degree of hydrophobic substitution	Cationic charge$^{\delta}$
Cat-hmHEC	high	+
Polyquaternium-10 (PQ-10) or cat-HEC*	none	+
Polyquaternium-67 (PQ-67)**	medium	+
Hydroxyethyl cellulose (HEC)***	none	0

$^{\delta}$ Cationic charge: "+" indicates with cationic charge; "0" indicates no cationic charge
*UCARE™ JR-30M Polymer
**SoftCAT™ SX-1300X Polymer quaternized hydroxyethyl cellulose (HEC) polymers with cationic substitution of trimethyl ammonium and dimethyldodecyl ammonium groups
*** CELLOSIZE™ PCG-10 Hydroxyethyl Cellulose

Heat damage procedure:

Hair tresses (2 g, medium brown virgin hair available from International Hair Importers) were wetted for 30 seconds in 37 °C distilled water, then a 9 wt% sodium lauryl sulfate (SLS) solution (0.2 g/g of hair) was massaged into the hair for 30 seconds before rinsing with water at rate of 0.4 L/min for 30 seconds and detangled with a brush; then the tress was given a final rinse with water at rate 0.4 L/min for 30 seconds. The hair tresses were then treated by applying at 0.15 g of a 0.1-1 wt% aqueous treatment solution of the active material per gram of hair and massaged for 1 min. The tresses were allowed to air-dry at room temperature for at least 12 hours at 25 °C, 50% RH prior to the heat treatment.

232 °C heat treatment:

Flat iron was preheated to 450 °F (232 °C) then the tresses were passed through the plates ten times for 10 seconds each with the flat iron. A full heat treatment cycle consists of 9% SLS wash, polymer treatment, and heat treatment ten times. The procedures were repeated for a total of 3 cycles. Once the third cycle was completed, the tresses were washed with 9% SLS (0.2 g/g of hair) for 30 seconds, rinsed with water for 1 min, and dried at room temperature, 50% RH for at least 12 hours prior to the analyses.

Differential scanning calorimetry (DSC):

Prior to the analysis, the hair was trimmed and submerged in water overnight to plasticize the hair and lower the keratin denaturation temperature below the decomposition temperature [13]. Samples were prepared by isolating at least two different sections of hair from each tress and trimming them into small (< 2 mm long) pieces. The entire length of the chosen hair section was cut up and randomly distributed on weighing paper to average any difference in hair properties along the length of the tress. A 10±3 mg sample was then taken from each mass of small hair pieces using tweezers. The samples were placed into a high-pressure stainless steel pan and distributed evenly on the bottom of the pan. To each pan, 18 mΩ water was added using a Rainin E4 XLS electronic pipette (SN: B737669585). The pans were visually inspected, and stray hairs were removed before sealing to ensure a tight seal. The pans were then press-sealed with a Viton O-ring and a stainless-steel lid and weighed for total starting mass. To allow the hair samples to equilibrate in hydration level, the sealed pans were allowed to sit for 12 hours at 25 °C. The samples were then analyzed by a TA Instruments Q2000 Differential Scanning Calorimeter (DSC) (SN: 1000-0094) paired with a Refrigerated Cooling System (RCS90) unit. The samples were analyzed by equilibrating at 40 °C then heating the samples to 200 °C at a 10 °C per minute ramp rate. During the sample analysis, the cell flow rate was 25 mL per minute of nitrogen. Instrumental software (TRIOS v4.4.0) was used to determine both the denaturation temperature (T_d) and the denaturation enthalpy (ΔH). The denaturation temperature was determined as the peak temperature of the endothermic transition and the denaturation enthalpy was determined by integrating the endothermic transition.

UV-Vis analysis of polymer residues on hair:

The quantification of the amount of cellulose polymers deposited onto hair was performed using diphenylamine assay [14]. All hair tresses were run in duplicate and the UV-Vis measurements were measured at least once per sample.

Approximately 100-200 mg of a treated hair tress was removed from the swatch and cut into 0.5 cm pieces. The entire length of the tress was used to ensure no discrimination from root to tip. The cut hair was placed in a tared test tube and the exact mass recorded. To the test tube was added 1 mL deionized water and 10 mL diphenylamine reagent (3.75 g diphenylamine in 150 mL glacial acetic acid and 90 mL 37% aqueous hydrochloric acid). A blank was prepared with 1 mL deionized water and 10 mL diphenylamine reagent. The test tubes were sealed with a rubber septum with a vent needle to avoid rupture. The sealed test tubes were placed in boiling water for one hour, removed from the water and allowed to cool to room temperature.

After running the blank, each sample was analyzed by UV-Vis from 325 to 900 nm on precision mode (Fisher GENESYS 150 spectrophotometer). To account for the variable baseline in the samples, an equation for a line was determined for each sample between two minimum points (473 nm and 741 nm). Using this equation, the baseline at 622 nm was calculated and subtracted from the measured value at 622 nm. This value was multiplied by 163.5 (slope of Beer’s law plot for Polymer PK) to determine the µg of polymer in the sample. This value was divided by the original mass of the hair tress sample to afford the µg polymer per g of hair.

Results and Discussion

Thermal protection of hair keratin by cellulosic polymer treatments

To reduce hair damage upon heat exposure, a series of conditioning cellulosic polymers were selected and screened for their thermal protective properties. Due to their high solubility in water, 0.1 and 1 w/w % of polymer in water were used and applied onto the hair tresses prior to the heat treatment. To mimic real-life applications, three cycles of hair washing, polymer treatment, and heat treatment (10 passes, 10 seconds each) were performed, and the tresses were washed with 9% SLS to remove excess polymer prior to the DSC analysis. Two thermal parameters, derived from the DSC endotherm, were used to assess hair damage: T_d of the helical protein and ΔH. T_d is used to characterize the thermal stability of the proteins in hair and measured from the peak temperature. ΔH measures the energy uptake for the unfolding of the alpha-helical structure during denaturation, and the value can be measured from the area under the curve. Ideally, the higher the T_d and ΔH, the stronger the hair fiber.

To effectively compare the results, % T_d and ΔH loss were calculated based on Equation *(1)* and *(2)*. The level of protein thermal protection was also calculated based on the difference in ΔH reduction between the untreated hair sample and the polymer pretreated hair sample, as shown in Equation *(3)*[15].

$$\%T_d\ loss = \frac{(T_{dV} - T_{dS})}{T_{dV}} \bullet 100 \qquad (1)$$

$$\%\Delta H\ loss = \frac{(\Delta H_V - \Delta H_S)}{\Delta H_V} \bullet 100 \qquad (2)$$

$$\%\ Protein\ protection = \frac{(\Delta H_{lossN} - \Delta H_{lossP})}{\Delta H_{lossN}} \bullet 100 \qquad (3)$$

Where T_{dV} = denaturation temperature of neat virgin hair without a thermal treatment

T_{dS} = denaturation temperature of thermally treated hair with or without polymer protectant

ΔH_V = denaturation enthalpy of neat virgin hair without a thermal treatment

ΔH_S = denaturation enthalpy of thermally treated hair with or without polymer protectant

ΔH_{lossN} = difference in ΔH between neat hair and thermally treated hair without a protectant

ΔH_{lossP} = difference in ΔH between neat hair and thermally treated hair with a protectant

When pretreating the hair with the conditioning polymers, a reduction in both T_d and ΔH was observed when compared to virgin hair without heat treatment. However, the reductions in both parameters are significantly less pronounced than for the thermally treated hair without a protectant (Table 2). Results clearly suggest that the polymer pretreatment provides heat protection to the hair fiber. This is likely due to a thin film formation which could act as a barrier to prevent the hair from over-heating (**Figure 6**). When screening 1 w/w % use level, cat-hmHEC polymer showed the highest T_d and ΔH values with the least amount of T_d and ΔH loss of 1.32 and 14.82%, respectively. Since ΔH is directly associated with the denaturation of the α-helical protein, 1% cat-hmHEC polymer provides ~63% thermal protection to the hair protein and reduces ~2.7 times the helical protein loss when compared to the hair without the protectant. When using cat-HEC polymer (PQ-10) (1%) which has a similar charge density and molecular weight but without a hydrophobic moiety, both T_d and ΔH were reduced significantly. In the absence of hydrophobicity, the level of protein denaturation increases ~2x in comparison with cat-hmHEC polymer at the same use level (1%). When using HEC which contains no cationic charge nor hydrophobic moieties, no significant difference in T_d and ΔH between HEC and cat-HEC polymers were observed. Results clearly suggest that a cationic charge has no impact on reducing damage from thermal treatment.

When using 1 w/w% PQ-67 Polymer, which contains dimethyldodecyl functionality, both T_d and ΔH values are lower than that of cat-hmHEC polymer but higher than PQ-10 or HEC polymers. The results are as expected since the level of hydrophobicity of PQ-67 is not nearly as high as that in cat-hmHEC polymer. It is hypothesized that a long alkyl chain together with an adequate degree of substitution may provide another layer of protection to the hair in comparison to PQ-10 and HEC which contains no hydrophobicity. This observation is consistent with the previous finding on the impact of hydrophobicity on the level of protection against protein thermal degradation [15].

It is noteworthy that when using 1 w/w % use level of conditioning polymer solution as a leave-in product, the treated hair had a strong and firm hold. In order to achieve a more natural hold with a soft feel, the use level was reduced to 0.1 w/w %. At this level, cat-hmHEC polymer still provided thermal protection against heat damage with similar ΔH and % ΔH loss to 1% PQ-10. The level of protein protection was reduced by ~2.7x when compared with 1% cat-hmHEC polymer. The T_d loss was also significantly higher than when using 1% polymer, indicating that the use level plays a crucial role in the thermal stability of the hair.

Table 2. Denaturation enthalpy (ΔH) and denaturation temperature (T_d) of non-thermally and thermally-treated medium brown virgin hair with and without polymer

Treatment on medium brown virgin hair		Average* ΔH (J/g)	ΔH stdv**	Average* T_d (°C)	T_d stdv
No heat; no treatment		22.06	0.45	152.56	0.16
Thermally treated hair at 232 °C	no treatment	13.21	1.29	141.99	0.24
	cat-hmHEC Polymer (0.1%)	15.25	0.76	145.53	0.26
	cat-hmHEC Polymer (1%)	18.79	0.82	150.55	0.84
	Cat-HEC or PQ-10 (1%)	15.76	1.13	148.54	0.27
	PQ-67 (1%)	17.05	0.70	149.3	0.48
	HEC (1%)	16.71	0.76	147.65	0.34

*Average of 5 measurements
**Stdv = standard deviation

Figure 1. T_d and ΔH loss of thermally treated hair at 232 °C. The results were calculated based on the hair without thermal treatment.

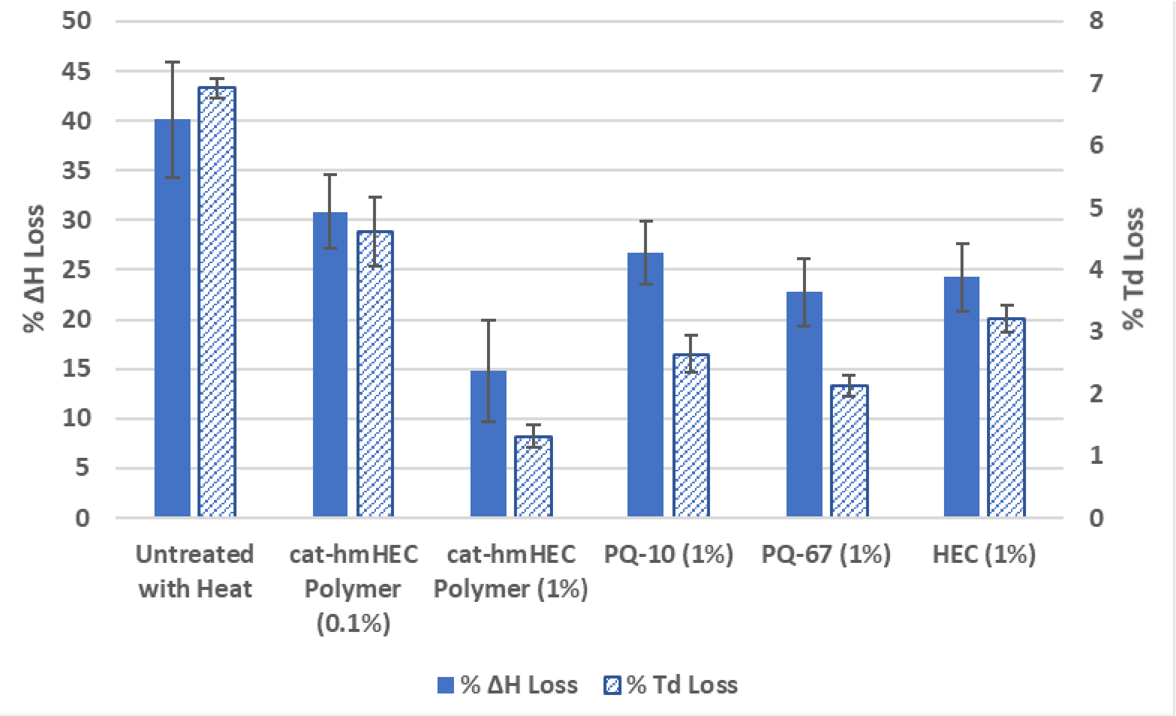


Figure 2 illustrates a plot of the level of protein protection with respect to the % T_d and ΔH loss. The size of the ball indicates the level of protein protection (%) as describe in Equation (3) and has an inverse relationship with the % loss of T_d and ΔH. cat-hmHEC polymer (at 1% use level) with the lowest T_d and ΔH % loss has the highest level of protein protection. On the other hand, the thermally treated hair without a protectant has the lowest level of protein protection, with the highest T_d and ΔH loss. Results also confirmed the 0.1 % use level of cat-hmHEC polymer provides moderately good protein protection as compared with the thermally treated hair without a protectant. Figure 3 depicts a plot of the level of protein protection with respect to the charge density and relative hydrophobicity of the cellulosic material. Unlike the charge density, the level of hydrophobicity has a major impact on the ability to protect proteins against thermal damage. The higher the hydrophobicity, the higher level of protein protection. While the chemistry allows for the tunability of the level of hydrophobicity, a much higher degree of substitution may cause an instability issue in water-based formulation [15-16].

Figure 2. Level of protein protection with respect to the % T_d and ΔH loss. The size of the ball indicates the level of protein protection.

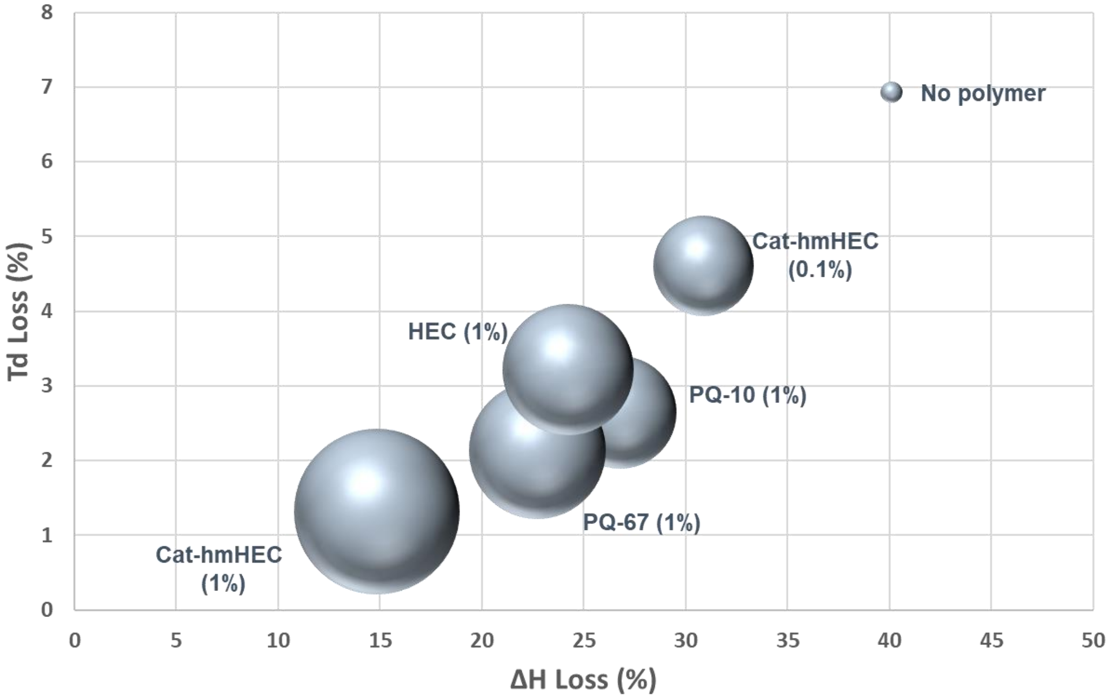
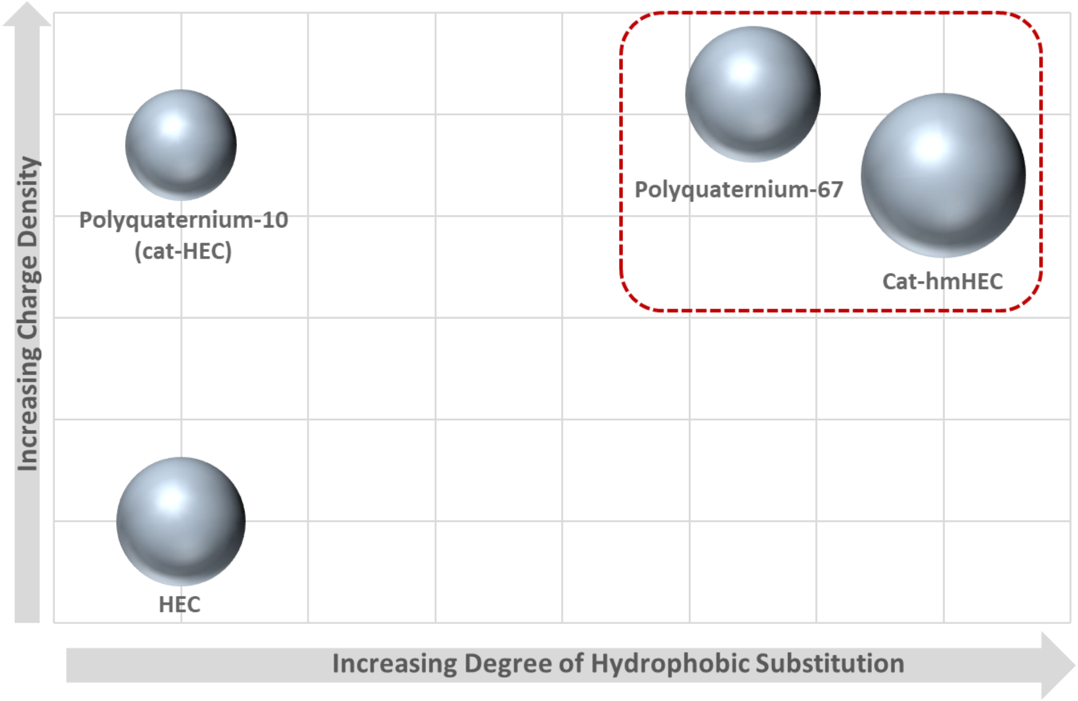


Figure 3. Level of protein protection with respect to charge density and relative hydrophobicity. The size of the ball indicates the level of protein protection.



In addition to the DSC analysis, the surface of the hair cuticle was visualized using SEM to identify the physical damage on hair after the heat treatment. Cuticle edge wear and occasional cracking were observed in both virgin hair with and without thermal treatment, likely due to physical abrasion during combing or hair treatment. (Figure 4). For the virgin hair with thermal treatment at 232 °C, noticeable micropores, bubbles, bumps, and spots on the hair cuticle surface were observed (Figure 5). This is likely due to multiple cycles of over-heating and a rapid dehydration of the hair fibers [15-17]. Such damage may increase the hair permeability, hence increasing the rate of water loss during heating [15]. For tresses treated with 1% cat-hmHEC polymer, the overall cuticle was intact with small shallow depressions in some areas of the hair shaft. Small bumps were also observed but not as pronounced as the thermally-treated virgin hair without polymer protection. It was noted that polymer film deposition is evident on the surface of the hair shaft even after the SLS wash (**Figure 6**).

Figure 4. SEM Images of untreated virgin hair and thermally treated hair. Raised bumps and micropores from a rapid dehydration are indicated by yellow arrows and circles, respectively.

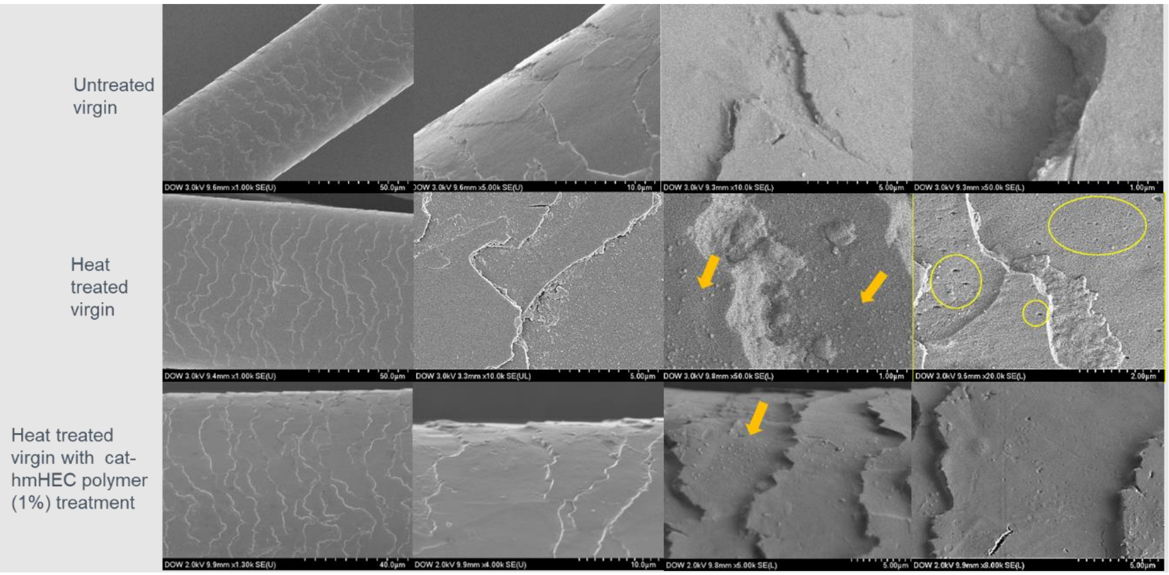
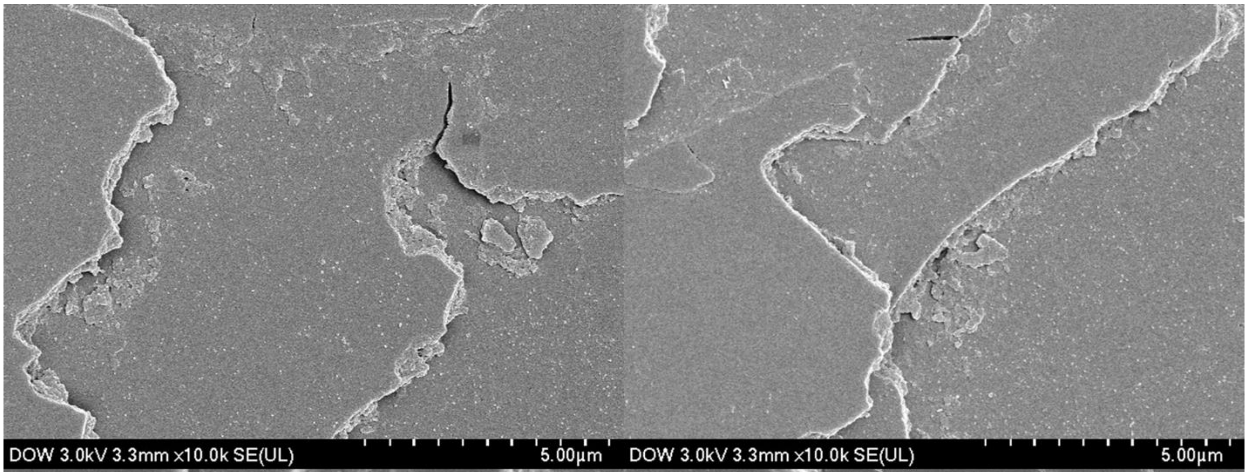


Figure 5. Thermally treated virgin hair at 232 °C for (10s x 10 passes)



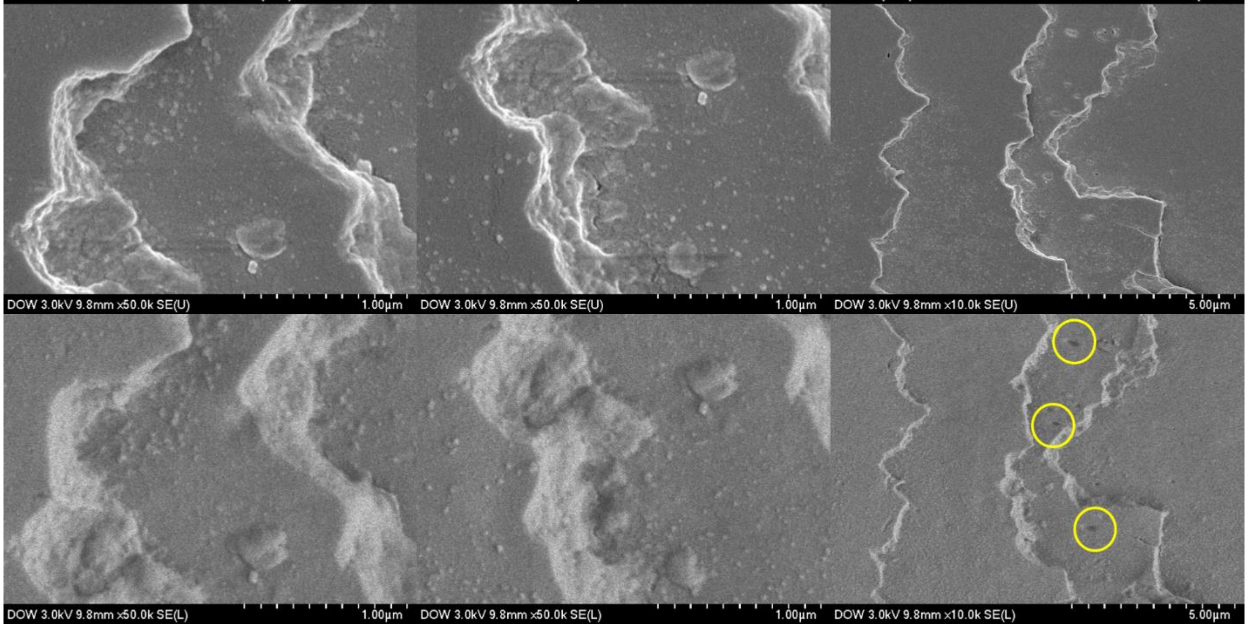
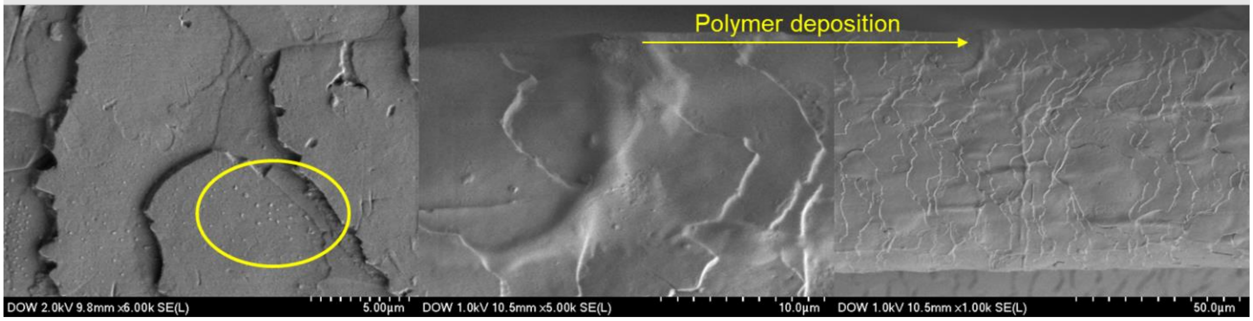
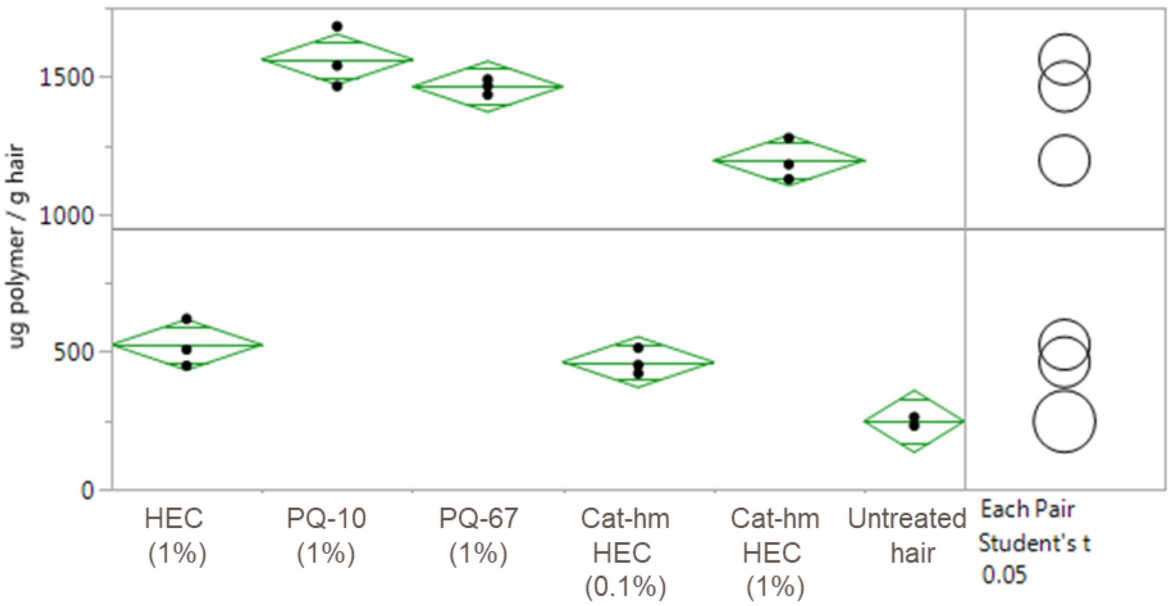


Figure 6. Thermally treated tresses with cat-hmHEC polymer (1%) – 232 °C. Patches of small white dots in these images are raised bumps. They are distinguished by bright 'lighting' on the right side and a shadow to the left in 'SE(L)' labelled images. Features that are darker on the right with brighter boundaries to the left are depressions of various types.



Although the tresses were washed with 9% SLS prior to thermal analysis, it was found that residue polymers still remained on the surface of the hair as analyzed by UV-Vis measurement (**Figure 7**). The highest concentration was found when 1% PQ-10 or PQ-67 was employed, with ~1500 µg of polymer per g of hair. After washing, cat-hmHEC polymer residue was significantly less when using the same starting use level, suggesting an ease of removal and less polymer build up after shampooing. When using 1% HEC, the residue level was found to be only ~500 µg/g of hair, slightly higher than that of the untreated hair. The SEM analysis also confirmed the presence of trace polymer on hair even after an SLS wash. This is likely because HEC contains no cationic charge which leads to a lack of retention of the polymer on the hair. When using 0.1% cat-hmHEC polymer, a low concentration of residue was observed as well. Moving forward with water-based formulation containing cationic polymer as a heat protectant, 0.1% cat-hmHEC polymer is therefore recommended as it provides a soft and natural feel with adequate thermal protection.

Figure 7. Analysis of the cellulosic residue on the hair surface by UV-Vis after washing with 9% SLS



Conclusion.

Modification of cellulosic polymers has enabled different features that provide unique benefits to hair applications. Varying structural parameters such as hydroxy and hydrophobic substitution significantly impact not only sensorial properties but also thermal properties. The polymer pretreatment provided significant reduction in T_d and ΔH loss in comparison to the thermally treated hair without a protectant. Among all the polymers that were screened in this study, cat-hmHEC polymer provided the highest level of thermal protection, and HEC and PQ-10 provided the least level of protection at the same use level (1 w/w %). Pretreatment of hair with the hydrophobically-modified HEC (cat-hmHEC and PQ-67 polymers) provided thermal protection to the hair surface resulting in a reduction in T_d and ΔH loss and an increase in the level of protein protection. Cationic charge didn't have a significant impact on reducing damage from thermal treatment (HEC vs PQ-10). While all the polymers used in this study were able to form films as shown by SEM, polymers containing hydrophobic substitution were found to provide another layer of thermal protection. This learning can be leveraged and applied to other types of polymer backbones to achieve similar thermal properties. It is therefore crucial to understand the structure-property-performance relationship to achieve performance.

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Conflict of Interest Statement. NONE.

References. All the references must be quoted numerically in the order in which they appear in the manuscript. This must be done in between square brackets [1].

Examples:

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