Study of hair surface energy and conditioning

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Synopsis

A new test method has been developed to determine surface energy of hair fibers through measurements of contact angles at two hair/liquid interfaces. By measuring changes in surface energy of the same hair fiber before and after a cosmetic treatment, effects of active ingredients and the performance of tested formulations can be evaluated.

The establishment of the method is based on Fowkes theory (1,2) described with two components, a dispersive and a non-dispersive component. The non-polar liquid used in this study was diiodomethane, and the polar liquid was benzyl alcohol. A Kruss 100 Tensiometer was used to measure contact angles of hair fibers. Virgin dark brown and regular bleached hairs were treated with selected conditioner formulations. Reductions in combing forces of hair tresses before and after respective treatments were correlated with decreases in average surface energy of hair fibers obtained from the corresponding tresses.

Experimental results indicate that the average surface energy of hair fibers treated with conditioners decreases and the hydrophobicity of the hair surface increases, the results correlate well with the reduction in combing forces after respective treatments. This research work provides a new methodology to evaluate/screen conditioning performance of hair care ingredients and formulations for development of better products.

INTRODUCTION

Surface energy is one of important physico-chemical properties of solid materials, as it impacts surface properties of the solid, such as wetting, spreading, and adhesive performance. Surface energy of hair affects how cosmetic treatments interact with hair surface, it can be used to judge the nature of the hair, as healthy hair always has lower surface energy compared to that of damaged hair. All cosmetic products applied onto hair surface actually change the surface energy of the hair. In order to improve hair conditioning performance, formulations should modify the treated hair surface and make it more hydrophobic with lower surface energy. Researchers from Textile Research Institute in Princeton have published several papers on studies of changes in wettability of keratin fibers after different treatments (3–5). The surface wettability or contact angle at the fiber/water interface is related to the surface energy, but not equal to that. Therefore, it is important to study changes in surface energy of hair fibers after different treatments.

Though measuring the surface energy of a liquid is simple and direct, because the surface energy of a liquid equals the surface tension of the liquid, but determining the surface energy of a solid is not as straightforward (2). There are several published articles that

describe the calculation of polymer surface energy through the measurement of the contact angle, by applying theories such as the Zisman theory, the Owens/Wendt theory, the Fowkes theory, and the Van Oss theory (2,6,7). Mr. Brown and his co-workers from Procter & Gamble Company disclosed a method to measure surface energy of hair fiber by using an image device (8). They measured contact angles of hair fiber in two solvents (99% + pure hexadecane and ultrapure water) and calculated surface energy according to Fowkes equations.

The Fowkes theory is a combinaton of three equations that describe the interfacial interactions between the liquid and the solid (2,6). The first equation is Young's equation:

$$\sigma_s = \sigma_{sL} + \sigma_L \cos\theta \tag{1}$$

where σ_s = total surface energy of the solid, σ_{SL} = the interfacial tension between the liquid and the solid, σ_L = the surface tension of the liquid, and θ = the contact angle at the liquid/ solid interface.

Another important equation used in the Fowkes theory is Dupre's adhesion energy:

$$I_{SL} = \sigma_S + \sigma_L - \sigma_{SL} \tag{2}$$

where I_{SL} is the adhesive energy between the liquid and the solid surface.

The Fowkes theory separates the adhesive energy into the dispersive component which is attributed to the non-polar interaction of the interface, and the polar component that is contributed by the polar interaction at the liquid and solid interface. Therefore, the adhesive energy equation (2) becomes equation (3):

$$I_{SL} = 2 \left[\left(\boldsymbol{\sigma}_{L}^{D} \, \boldsymbol{\sigma}_{S}^{D} \right)^{1/2} + \left(\boldsymbol{\sigma}_{L}^{P} \, \boldsymbol{\sigma}_{S}^{P} \right)^{1/2} \right]$$
(3)

in which the interfacial tension variable is eliminated from the equation, and the combination of equations (1), (2), and (3) yields the Fowkes equation (4):

$$\left(\boldsymbol{\sigma}_{L}^{D}\boldsymbol{\sigma}_{S}^{D}\right)^{1/2} + \left(\boldsymbol{\sigma}_{L}^{P}\boldsymbol{\sigma}_{S}^{P}\right)^{1/2} = \boldsymbol{\sigma}_{L}\left(\cos\theta + 1\right)/2 \tag{4}$$

in which, $\mathbf{\sigma}_{L}^{D}$ = the dispersive component of the surface tension of the liquid, $\mathbf{\sigma}_{s}^{D}$ = the dispersive component of the surface energy of the solid, $\mathbf{\sigma}_{L}^{P}$ = the polar component of the surface tension of the liquid, $\mathbf{\sigma}_{s}^{P}$ = the polar component of the surface energy of the solid, the total surface energy ($\mathbf{\sigma}_{s}$) of a solid material is the sum of the dispersive surface energy ($\mathbf{\sigma}_{s}^{D}$), and the polar surface energy ($\mathbf{\sigma}_{s}^{P}$), is as described in equation (5):

$$\sigma_s = \sigma_s^{\ D} + \sigma_s^{\ P} \tag{5}$$

To use the Fowkes equation to calculate the surface energy of a solid surface, the contact angle of the solid needs to be measured in tow liquid probes. One recommended liquid probe is Diiodomethane ($\sigma_L = \sigma_L^D = 50.8 \text{ mN/m}$), which has only dispersive component

Purchased for the exclusive use of nofirst nolast (unknown) From: SCC Media Library & Resource Center (library.scconline.org) of the surface tension, and the other liquid probe should have both the dispersive and polar components of the surface tension, such as water ($\sigma_L^P = 46.4 \text{ mN/m}, \sigma_L^D = 26.4 \text{ mN/m}$), or benzyl alcohol ($\sigma_L^P = 11.4 \text{ mN/m}, \sigma_L^D = 28.6 \text{ mN/m}$). The contact angle values measured from diiodomethane are used to calculate the dispersive component of the solid surface energy, and the contact angle values measured from water or benzyl alcohol are applied to calculate the polar component of the surface energy (2,6,7).

In previously published articles (2,6), surface energies of common polymer solids were calculated using the theories mentioned above and the surface energy data of different types of hair were also cited in the literature (9). In addition, the contact angle values of hair fibers have been used to validate the hydrophobic/hydrophilic change of the hair before and after cosmetic treatment (10).

Professor Bhushan and his colleagues have published several papers to explore nanotribological characterization of hair (11,12), surface energy data of different hairs and changes in surface energy of hair fibers after different treatments were also circulated (8). But till now, there is no publication studying correlations between changes in the micro-scale property of hair-surface energy and changes in the macro-scale property of the hair tresses combing force. In this paper, a method of determining the surface energy of hair fiber samples is revealed. The changes in average surface energy of hair fibers before and after conditioner treatment were correlated to the changes in combing forces of corresponding tresses. Experimental results verified that a decrease in hair surface energy can be used to evaluate or screen the performance of cosmetic ingredients and formulations.

EXPERIMENTAL

MATERIALS AND INSTRUMENTS

- KRŰSS Processor Tensiometer K100MK2, from KRŰSS, USA
- Laser Scanning Micrometer, Mitutoyo LSM-5000, from Mitutoyo, Japan
- Miniature Tensile Tester MTT-175 and MTT-160, from Dia-Stron Instruments, UK
- Virgin brown and regular bleached hair were purchased from International Hair Importers, Inc., New York.
- Quaternium-91 (and) cetrimonium methosulfate (and) cetearyl alcohol (Trade name: CrodazosoftTM DBQ, Croda Inc., Edison, NJ)
- Behentrimonium methosulfate (and) cetyl alcohol (and) butylene glycol (Trade name: Incroquat[™] Behenyl TMS-50, Croda Inc., Edison, NJ)
- Conditioner-A contains 6.00% of Quaternium-91 (and) cetrimonium methosulfate (and) cetearyl alcohol, 0.80% of Neolone CAPG, and the rest was balanced with DI-water.
- Conditioner-B contains 6.00% of behentrimonium methosulfate (and) cetyl alcohol (and) butylene glycol, 0.10% of Neolone 950, and the rest was made up with DI-water.

CONTACT ANGLE MEASUREMENT

- Virgin brown and regular bleached hair tresses were prewashed with 10% sodium lauryl sulphate.
- Thirty hair fibers were randomly selected, crimped onto two brass tabs, and the central diameter of the hair fiber was measured using a laser scanning micrometer.

- Cut the hair fiber into two parts: A and B. Part A was used as control without any treatment, and part B was treated with testing conditioners.
- Dynamic advancing contact angle of single hair fiber was measured using a KRŰSS Processor Tensiometer K100MK2. The value of a determined contact angle in diiodomethane was used to calculate the dispersive component of the surface energy, and the measured value of contact angle in benzyl alcohol was used to calculate the polar component of the surface energy.
- The total surface energy of the hair fiber is the sum of the dispersive and polar components.

COMBING FORCE MEASUREMENT

- Hair tress width is 1.2 cm, and the length is 20 cm. Virgin Brown and Regular Bleached hair tresses were prewashed with 10% sodium lauryl sulphate (SLS) before use.
- Apply 2 ml of 10% SLS solution to the hair tress and manage it gently for 1 minute. Work the tress from the top to the bottom to avoid tangling.
- Rinse the tress with running tap water for 1 minute. Let the tap water run down the swatch from the top to the bottom to avoid tangling.
- For each formulation, five hair tresses were used for combing force measurements before and after respective treatment.
- Wet combing forces were determined at room temperature and dry combing force measurements were performed in a chamber with a constant humidity level of 65%.

Percentage changes in dry or wet combing forces of the same tress before and after respective treatment were calculated and averaged for five hair tresses.

RESULTS AND DISCUSSION

CHANGE IN AVERAGE CONTACT ANGLE VALUES

Contact angle values of hair samples treated with conditioner-A were summarized in Figures 1 and 2, respectively, for bleached and virgin hair. Contact angle values of conditioner-B treated hair were illustrated in Figures 3 and 4, respectively. The lower bars represent contact angle values of the control hair, the taller bars show contact angle values of the treated hair samples. Two bars on the left side of each figure indicate contact angle values measured at the diiodomethane/air interface, and the two bars on the right side represent the contact angle values measured at the air/benzyl alcohol interface.

It can be seen that average contact angle values of conditioner-A treated bleached hair fibers increased by 25.07% in diiodomethane, and 21.97% in benzyl alcohol, respectively. While the average contact angle values of conditioner-A treated virgin hair increased by 12.54% in diiodomethane, and 25.04% in benzyl alcohol, respectively. It is clear that hair surface became more hydrophobic in both liquid probes in comparsion to the control samples without any treatment.

As shown in Figures 3 and 4, the surface of hair samples treated with conditioner-B also became more hydrophobic. Average contact angle values of conditioner-B treated bleached hair raised by 25.54% in diiodomethane and 29.64% in benzyl alcohol, respectively.



Figure 1. Contact angle values of the control and conditioner-A treated bleached hair.



Figure 2. Contact angle values of the control and conditioner-A treated virgin hair.

However, the percentage increases in average contact angle for conditioner-B treated virgin hair is only 13.37% in diiodomethane, and 15.80% in benzyl alcohol. These changes are significantly less than those for the bleached hair at the same liquid /air interface.

The differences in percentage changes of average contact angles between conditioner-A and conditioner-B treated hair fibers may be attributed to the different molecular structure of active ingredients in each formulation. Quaternium-91 in conditioner-A has two long alkyl carbon chains (C_{22}) and delocalized positive charge, which made this ingredient a very good conditioning agent on both virgin and bleached hair, whereas behetrimonium



Figure 3. Contact angle values of the control and conditioner-B treated bleached hair.



Figure 4. Contact angle values of the control and conditioner-B treated virgin hair.

methosulfate in conditioner-B has higher positive charge density, and certainly has strong interaction with the damaged, negative-charged hair surface such as bleached hair (7). Therefore, conditioner-B showed a better conditioning effect on the bleached hair with a larger percentage increase of the contact angle values after the treatment.

CHANGE IN SURFACE ENERGY AFTER CONDITIONING

Data of calculated surface energy of hair fibers are summarized in Tables I and II.

The surface energy of conditioner-A treated bleached and virgin hair reduced by 29.06% and 31.77%, respectively (Table I), which indicated that the conditioner-A demonstrated the similar conditioning effect on both hair types, and these results corresponded well with results on percentage changes in contact angles of conditioner-A treated bleached and virgin hairs.

Reductions in hair surface energy after conditioner-B treatment are summarized in Table II. It is observed that the average surface energy decreased by 33.72% and 27.64%,

Table I Calculated Surface Energy of Conditioner-A Treated Bleached and Virgin Hair				
Bleached hair	Control	Treated	% Change	
Polar surface energy, σ_{S}^{P} (mJ/m ²)	2.18	1.79	-17.98	
Dispersive surface energy, σ_S^{D} (mJ/m ²)	27.65	19.38	-29.91	
Total surface energy, $\sigma_{S} = \sigma_{S}^{P} + \sigma_{S}^{D} (mJ/m^{2})$	29.83	21.17	-29.06	
Virgin Hair	Control	Treated	% Change	
Polar surface energy, σ_{S}^{P} (mJ/m ²)	2.48	1.77	-28.68	
Dispersive surface energy, σ_S^{D} (mJ/m ²)	16.41	11.12	-32.24	
Total surface energy, $\sigma_S = \sigma_S^{P} + \sigma_S^{D} (mJ/m^2)$	18.89	12.89	-31.77	

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Calculated Surface Energy of Conditioner-B Treated Bleached and Virgin Hair				
Bleached hair	Control	Treated	% Change	
Polar surface energy, $\sigma_{S}^{P} (mJ/m^{2})$	1.87	1.79	-4.39	
Dispersive surface energy, $\sigma_{S}^{D} (mJ/m^{2})$	25.03	16.04	-35.92	
Total surface energy, $\sigma_S = \sigma_S^{P} + \sigma_S^{D} (mJ/m^2)$	29.90	17.83	-33.72	
Virgin hair	Control	Treated	% Change	
Polar surface energy, $\sigma_{S}^{P} (mJ/m^{2})$	0.64	0.45	-28.87	
Dispersive surface energy, $\sigma_{S}^{D} (mJ/m^{2})$	17.83	12.91	-27.59	
Total surface energy, $\sigma_{S} = \sigma_{S}^{P} + \sigma_{S}^{D} (mJ/m^{2})$	18.47	13.36	-27.64	

Table II

respectively, for bleached hair and virgin hair. It is clear that conditioner-B showed better conditioning performance on the bleached hair with damaged hair surface.

According to the data of dispersive and polar components of the hair surface energy in Tables I and II, the polar component of the hair surface energy is less than 15% of the total surface energy for both controls and treated hair samples. This indicates that the major part of hair surface energy can be attributed to non-polar interactions on hair surface. Therefore, we may just use the change in dispersive surface energy to evaluate the conditioning effect of formulations.

CHANGE IN COMBING FORCE AFTER CONDITIONING

In order to study correlations between changes in hair surface energy and combing force, both bleached and virgin hair tresses were treated with conditioner-A and conditioner-B, separately. Percentage changes in dry and wet combing forces after conditioner-A treatment are demonstrated in Figures 5 and 6, and results for conditioner-B treatment are presented in Figures 7 and 8.

As is shown in Figures 5 and 6, reductions in dry and wet combing forces of conditioner-A treated bleached and virgin hair are very close, which suggested that the conditioner-A had similar conditioning effect on both hair types. These results are consistent with those obtained from measurements of contact angles and the calculated hair surface energy after conditioner-A treatment.

Percentage changes in combing forces of bleached and virgin hair after conditioner-B treatment are presented in Figures 7 and 8. It can be seen that reductions in both dry and wet combing forces are more pronounced for bleached hair than for virgin hair. These results indicated that conditioner-B exhibited better conditioning effect on bleached hair, which corresponded well with those results obtained from reductions in hair surface energy.



Figure 5. Reductions in dry combing forces of conditioner-A treated hair.



Figure 6. Reductions in wet combing forces of conditioner-A treated hair.



Figure 7. Reductions in dry combing forces of conditioner-B treated hair.



Figure 8. Reductions in wet combing forces of conditioner-B treated hair.

CORRELATION BETWEEN REDUCTION IN SURFACE ENERGY AND DECREASE IN COMBING FORCE

Surface energy can be used as an indicator of surface reactivity. Higher the surface energy, more hydrophilic the hair surface, and stronger interactions between hair and water and between hair fibers each other will be. These will generate larger combing forcers during combing processes. Therefore, it is of our interest to establish correlations between reduction in surface energy and decrease in dry/wet combing forces of conditioner-treated hair samples. In this study, bleached and virgin hair were used and treated with conditioners A and B separately. Percentage changes in surface energy, dry combing forces, and wet combing forces on both bleached and virgin hair are plotted together in Figures 9 and 10, correspondingly, for conditioners A and B.

It can be seen from Figure 9 that the average surface energy of conditioner-A treated virgin and bleached hair reduced about 30%, and corresponding dry and wet combing forces of treated hair tresses decreased about 70% and 90%, respectively.

In Figure 10, the reduction in surface energy of conditioner-B treated bleached hair is 33.72%, which is more than the 27.64% for virgin hair. The decrease in dry combing forces for the bleached hair is 71.34%, which is much higher than the 34.96% for the virgin hair. The same trend is observed on reductions in wet combing forces between bleached and virgin hair.



Figure 9. Reduction of surface energy vs combing force for conditioner-A treated hair.



Figure 10. Reduction of surface energy vs combing force for conditioner-B treated hair.

CONCLUSIONS

Based on these experimental results, we may conclude:

- 1. Hair surface energy can be determined by using the Fowkes theory in a two-component liquid system.
- 2. After conditioner treatment, the combing forces of hair tresses reduced with a decrease in average hair surface energy.
- 3. The percentage reduction in average surface energy of treated hair fibers depends on the applied conditioner formulation and the type of hair.
- 4. The percentage decrease in dry/wet combing forces of cosmetically treated hair tresses also depends on the applied conditioner and the type of hair.
- 5. Determination of change in average surface energy of cosmetically treated hair samples can be used to evaluate/screen the conditioning performance of applied formulations (ingredients).

ACKNOWLEDGMENTS

The authors thank Mr. Abhijit Bidaye and Mr. Scott Cardinali of Croda Application Group for providing conditioner formulations. They thank the Research Director, Mr. Abel Pereira, and the Vice President of R&D, Dr. Rob Comber, for their support of the project.

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