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Silicones as conditioning agents in shampoos

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Synopsis

A one-step shampoo, generally called a "2 in 1" shampoo, exerting both cleansing and conditioning functions, differs to a great degree from conventional shampoo products, with its superb conditioning effects eliminating the necessity of a further conditioning step. Conditioning agents especially effective in such types of products are silicones, especially dimethicones with high molecular weight, dimethicone copolyol with low hydrophilic-lipophilic balance (HLB), and amodimethicone. In this work, the conditioning effects of these silicones are discussed in terms of the surface deposition and alteration in hair surface characteristics by measuring the kinetic frictional coefficient of hair fibers in relation to the chemical types and the molecular weight of silicones. The improvement in surface kinetic characteristics was primarily noted with dimethicones with high molecular weight. Dimethicone copolyol with low HLB lowered the kinetic friction of the wet hair surface by forming liquid crystals. Amodimethicone improved manageability of hair by adsorbing strongly onto the damaged, and therefore more polarized, hair cuticles, which facilitated hair styling without blow-drying.

INTRODUCTION

The use of silicones as lubricating and hydrophobic agents is found in a number of hair care products, e.g., shampoos, rinse conditioners, conditioners, hair sprays, styling mousses, setting lotions, hair colorings, permanent wave solutions, etc. Ease in combing, as well as a soft and smooth feeling without greasiness is the most valuable benefit obtained with silicones in hair care products. Another important factor is that silicones are non-toxic and non-irritating, and essentially safe.

In the present day, approximately 40% of Japanese females wash their hair daily; with younger generations this figure rises to approximately 70%. Therefore, a one-step shampoo, generally called a "2 in 1" shampoo, with double functions of shampoo and conditioner, is highly beneficial to these users for its ease and convenience. While its foaming and cleansing performance is comparable to an ordinary conditioning shampoo, the conditioning effect of a "2 in 1" shampoo is far greater than that of an ordinary conditioning shampoo. The groups of conditioning agents utilized in a "2 in 1" shampoo include silicones, hydrocarbon oils, fatty alcohols, cationic polymers, and cationic surfactants. There are some types of silicones that are especially effective as conditioners in detergent systems.

In this work, the conditioning effects of dimethicone, dimethicone copolyol, and amodimethicone are investigated. The performance of these silicones is discussed in terms of silicone deposition onto hair surface and alteration in the characteristics of hair.

EXPERIMENTAL

MATERIALS

Samples of silicone were obtained from Shin-etsu Chemical Co. (KF-96, X-21-7501G, KF6005, X-22-4110, and X-22-4104), Dow Corning Toray Silicone Co. (SH200, SH377X, and SM8702C), and Toshiba Silicone Co. (TSF451). All of the chemical ingredients for formulating shampoos were of commercial grade and were utilized without further purification. Table I shows the abbreviated designations for the silicones utilized.

METHODS

The following analytical instruments equipped with standard-type laboratory apparatuses were utilized: a scanning electron microscope (JEOL JSM-840), an electron probe microanalyzer (Tracor Tothern TN-503), an inductively coupled plasma (ICP) emission spectrometer (Seiko Instruments & Electronics Ltd. SPS-1200A), and a kinetic frictional coefficient meter (Nippon Rheologykiki Co., Type NRF-II). The method of determination of the critical surface tension of hair, estimated from the wetting force and the kinetic frictional coefficient measurement on a rotating nylon pulley, was done in accordance with the method described elsewhere (1). Measurement of dynamic combing force (2) during the shampooing process was performed with the modified combing method as described previously (1,3).

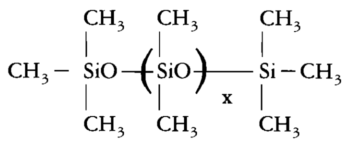
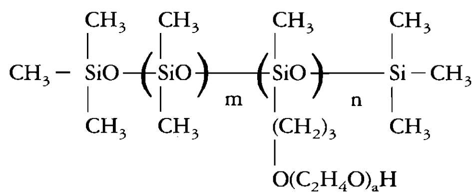
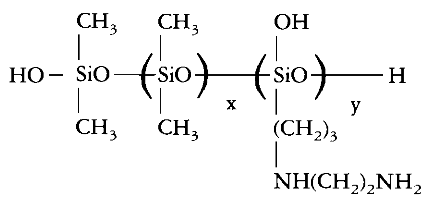
The procedure for determining silicone deposition is as follows: Approximately 0.5 g of hair sample, normal Japanese female hair with no history of chemical treatment, was extracted twice with 50 ml of chloroform for 20 min. The chloroform was removed by using an evaporator, and was replaced with 5 to 20 ml of methyl isobutyl ketone (MIBK) in order to dissolve the silicone. This solution was analyzed with an ICP emission spectrometer. Correction of silicone deposition on the untreated hair was conducted by analyzing hair samples that were not subjected to silicone deposition study.

RESULTS AND DISCUSSION

DIMETHICONES (POLYDIMETHYLSILOXANES)

Polydimethylsiloxanes (PDMS), also called dimethicones, were among the first commercially available silicone products. PDMS, having excellent lubricating properties and being utterly water-insoluble, form very hydrophobic films on the hair surface, and this is the reason why PDMS are frequently found in rinse conditioners, hair sprays, and styling mousses. Figure 1 shows the kinetic frictional coefficient (μ_k) of hair fibers treated with PDMS of various molecular weights (Mw). It can be seen from the figure that the formation of PDMS film on the hair surface causes a decrease in μ_k values, and

Table I
Silicones Used in This Work and Their Abbreviations

Name	Structures	Abbreviations	(trade name)
Dimethicones (polydimethyl-siloxanes)		PDMS	(KF-96) (SH200) (TSF451) (X-21-7501G)
Dimethicone copolyols (silicone glycol copolymers)		POES	(SH377X) (KF6005) (X-22-4104) (X-22-4110)
Amodimethicone (aminofunctional silicones)		ADMS	(SM8702C)

the magnitude is dependent on the Mw of PDMS (the μ_k with untreated hair is 0.18). The μ_k values increase in linear relation to the Mw, but unexpectedly start to decrease when the Mw exceeds the value of approximately 2×10^4. PDMS with extremely high Mw (Mw exceeding 10^5) are especially effective in changing the lubricity of hair surface

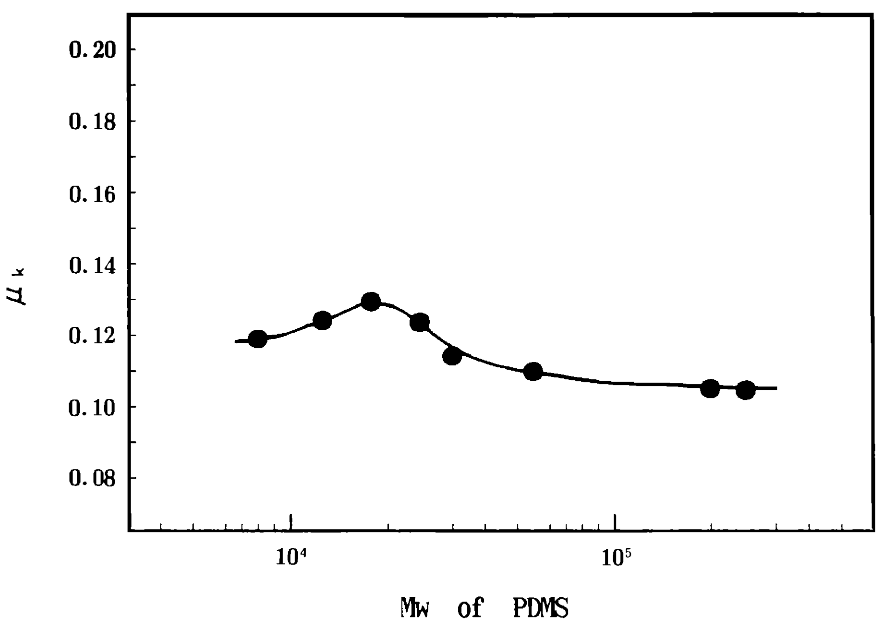


Figure 1. Effects of molecular weight of PDMS on the kinetic frictional coefficient of dry hair fibers.

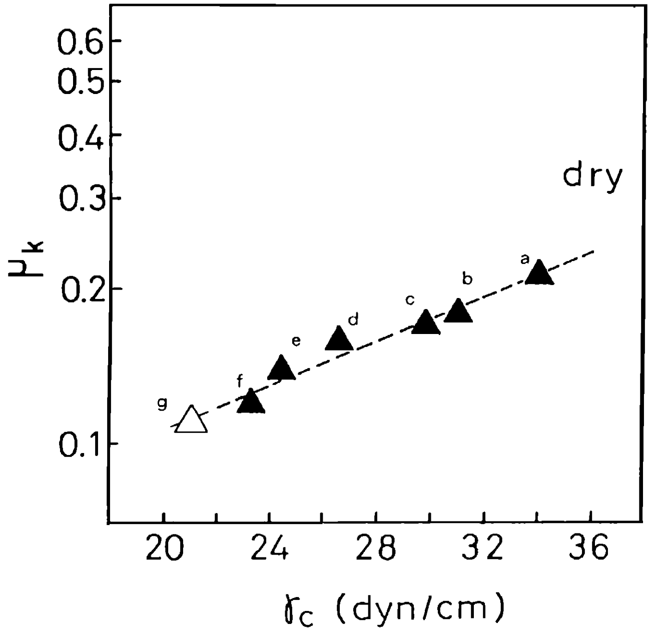


Figure 2. Plots of kinetic frictional coefficient vs critical surface tension for dry hair: a, clean bleached hair; b, clean normal hair; c, n-C_{18}TAC; d, n-C_{22}TAC; e, 2n-C_{18}DAC; f, g-C_{28}TAC (▲, reference 1); g, PDMS (△).

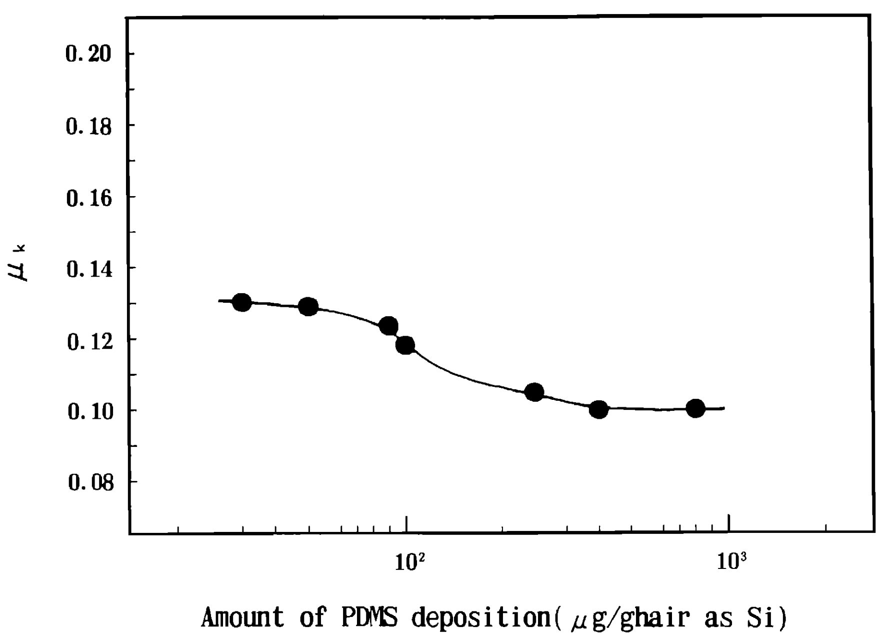


Figure 3. Effects of amount of PDMS (Mw $= 22 \times 10^4$) deposition on the kinetic frictional coefficient of dry hair fibers.

Table II
HLB Values and Solution Behaviors of POES

Dimethylsiloxane units: m	Polyoxyethylene units: n	Ethylene oxide mole: a	HLB value calc.*	Solubility in water at 25°C	Surface tension (dyn/cm)
60	3	4	3	Insoluble (oil)	—
75	3	11	5	Dispersible (L.C.**)	20.2
45	3	11	6	Dispersible (L.C.**)	20.2
25	3	11	8	Dispersible (emulsion)	20.7
6	3	14	13	Soluble (clear)	22.0

* Calculation of HLB: (weight percent of polyoxyethylene units) ÷ 5.
** L.C., liquid crystal.

with its low μ_k. The mechanism of the μ_k increases and then suddenly decreases in relation to the growing Mw values, and this may be explained by the effect of the viscosity. With increasing viscosity, μ_k also increases, but after exceeding the critical point where the PDMS films take on more solid-like form, the values start to decrease.

The relation between the μ_k and critical surface tension (γ_c) of hair fibers treated with cationic surfactants (1) and PDMS is plotted in Figure 2. The surface energy decreases, causing low adhesion and consequently low μ_k, when coverage of the hair surface with lubricant is complete. In the case of the hair surfaces treated with cationic surfactants, the effect on μ_k decrease was explained in terms of the amount of surfactant sorbed onto the hair (1). It is clearly shown that PDMS, forming hydrophobic and lubricating thin

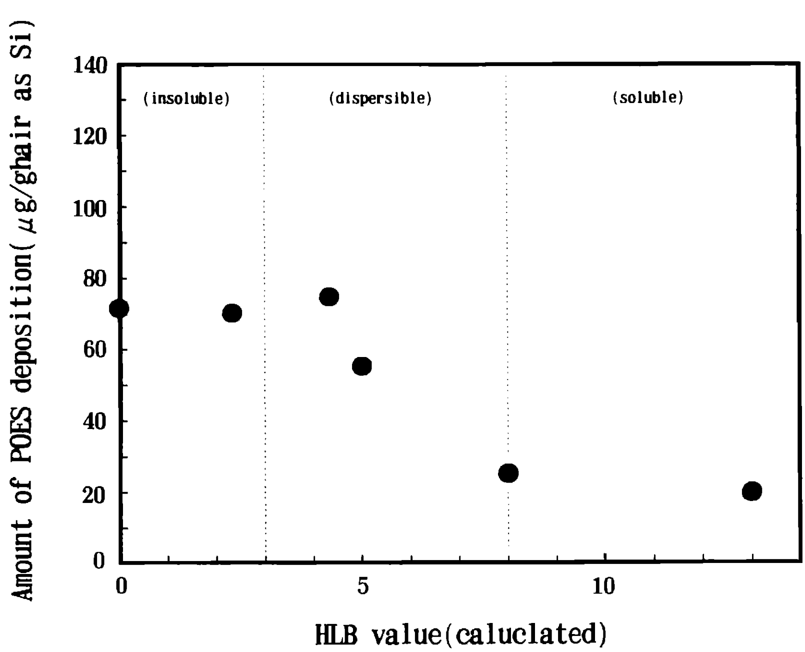


Figure 4. Plots of amount of POES deposition vs HLB value. The hair samples were treated with model shampoo (disodium polyoxyethylenelaurylethersulfosuccinate/amidoaminoacid triethanolamine/POES = 12/8/4 wt%).

films of hair surface, is more effective than cationic surfactants in improving the surface characteristics of hair.

Figure 3 shows the amount of PDMS deposited on hair surface and the effect on μ_k. The μ_k values were found to be depressed when the amount as Si deposited exceeded approximately 100 μg/g hair. This result may suggest that the amount of PDMS sufficient to form the film, which persists on the hair surface under the mechanical friction, is probably more than 100 μg/g hair.

DIMETHICONE COPOLYOLS (SILICONE GLYCOL COPOLYMERS)

With dimethicone copolyols (POES), some methyl groups attached to silicon have been replaced by polyether side chains, namely ethylene oxide or propylene oxide polymers or the copolymer of these. Since most POES contain enough glycol to be water-soluble, they are particularly useful in shampoo formulations requiring clarity. The chemical structures, the HLB values calculated, water solubility, and surface tension of various POES are listed in Table II.

POES with lower HLB values are not water-soluble, and in this sense they become similar to PDMS. With the addition of polyoxyethylene units and the reduction of

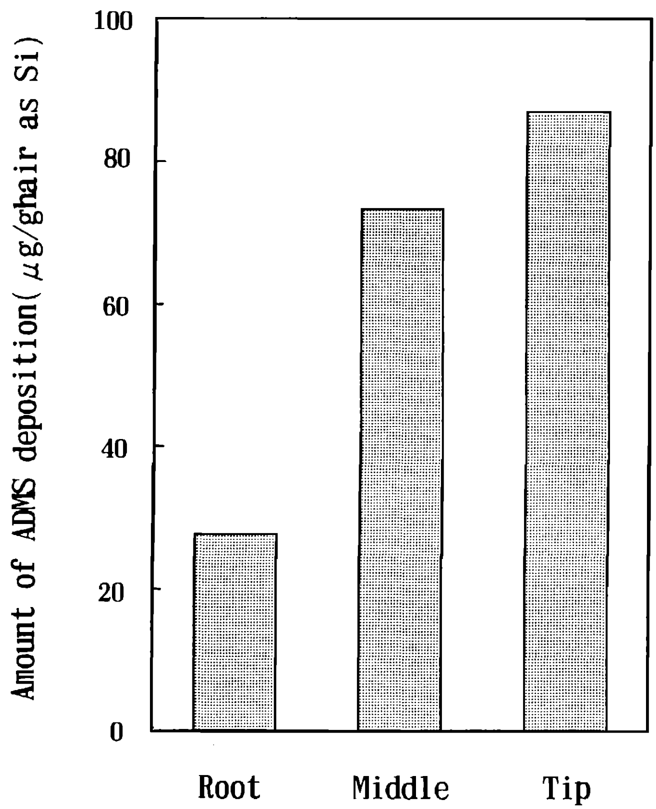


Figure 5. Effects of hair parts on amount of ADMS deposition, treated with model shampoo containing 0.2 wt% ADMS.

dimethylsiloxane units, both increasing the HLB values, these POES become dispersible and then finally water-soluble. In the case of the solution of POES with HLB values ranging from 5 to 6, liquid crystal formation was observed with a cross-polarizing microscope. With ordinary nonionic surfactants with polyoxyethylene chains, aqueous solutions are known to form lyotropic liquid crystals at optimum HLB (4). This solution behavior of POES bears fundamental similarity to that of organic surfactants, with the hydrophobic hydrocarbon groups being replaced by hydrophobic dimethylsiloxane groups.

The amount of POES deposition on hair treated with the model shampoo, containing 4 wt% POES, is plotted in relation to the HLB values in Figure 4. The samples with higher HLB scarcely remained on hair after being rinsed with water, and this is because of their high hydrophilicity. However, the samples of POES with lower HLB, dispersed in water, behaved almost identically to the PDMS as far as the amount of deposition is concerned. This result implies that the hydrophobic interaction between dimethylsiloxane units and hair surface plays an important role in the sorption behavior of silicones on hair. Therefore, the POES containing sufficient polyoxyethylene units to be water-soluble provide only a subtle conditioning effect, while POES with low HLB provide a light conditioning effect because of their deposition properties.

AMODIMETHICONE (AMINOFUNCTIONAL SILICONES)

One of the newest groups of silicones is the aminofunctional silicone polymers (ADMS),

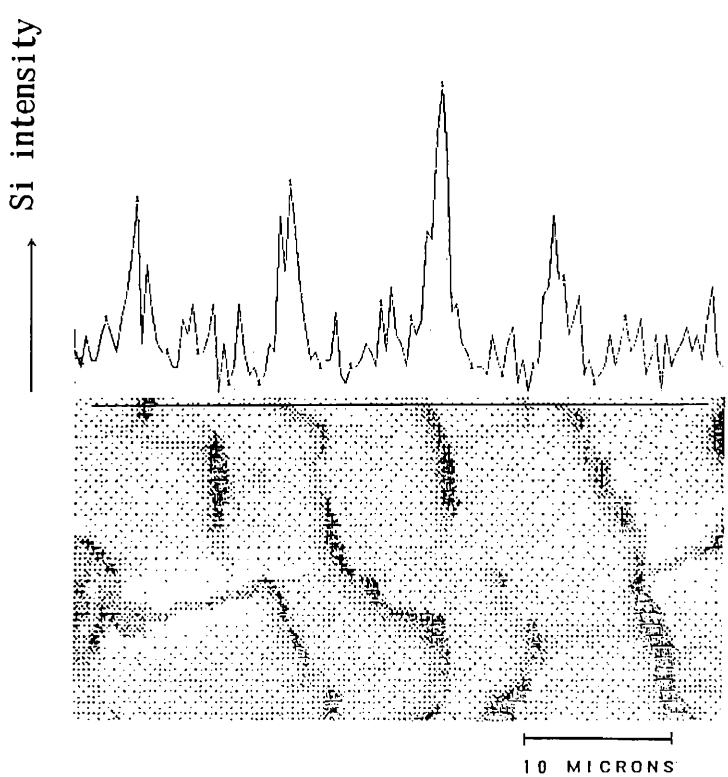


Figure 6. The distribution of Si atom on the hair surface by EPMA (line analysis). The hair sample was treated with 0.2 wt% ADMS emulsion.

in which the methyl groups attached to the dimethyl siloxane polymers are partly replaced with organic amine groups. Recently, Wendel and Disapio (5) have shown that ADMS tend to deposit on hair twice as much as dimethiconol and that the ADMS deposited are resistant to cycles of hair wash with shampoo. This measurement was conducted using a technique called electron spectroscopy for chemical analysis (ESCA).

In this paper, deposition characteristics were further investigated in greater detail by dividing long hair of approximately 70 cm into three parts, root parts, middle parts, and tip parts, and comparing deposition of ADMS on these parts. Figure 5 shows that the deposition amount on hair was less at the root part, moderate at the middle part, and considerably higher at the tip part. Further, the microscopic distribution of Si-atom on the hair, determined with an electron probe microanalyzer (EPMA) is shown in Figure 6. The result in Figure 6 indicates that ADMS, having stronger affinity to the negatively charged site, are selectively adsorbed on the edges of cuticles of hair. Figure 7 shows the scanning electron microscope (SEM) photograph of cuticle scales and the schematic diagram of the longitudinal slice through the hair surface. Mechanical wearing of the hair surface, caused by brushing, combing, towelling, and other general handling causes the cuticle scale edges to gradually chip away. In Figure 7a, the fractured scale edges and partly exposed endocuticle are shown. Endocuticle contains very little cystine, but, on the other hand, it is rich in acidic and basic amino acid residues, and it swells in contact with water (6). The higher amount of ADMS adsorbed at the hair tip seems to be related to hair surface conditions, which became more hydrophilic due to the damages. By this selective adsorbing characteristic of ADMS, physical properties of the surface of the damaged cuticles are expected to improve with application of ADMS.

APPLICATION OF SILICONES IN "2 IN 1" SHAMPOOS

PDMS, POES, and ADMS are expected to be especially effective as conditioning agents in "2 in 1" shampoos. The influence of silicones on the foaming properties is shown in Figure 8. A decrease in foam by the addition of PDMS may have resulted from the less

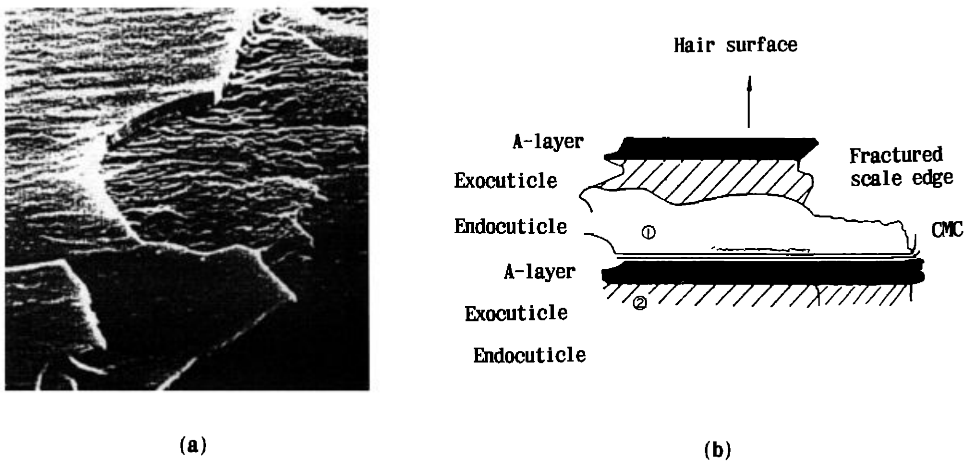


Figure 7. Scanning electron microphotograph of cuticle scales (a), and schematic diagram of the longitudinal slice through the hair surface (b).

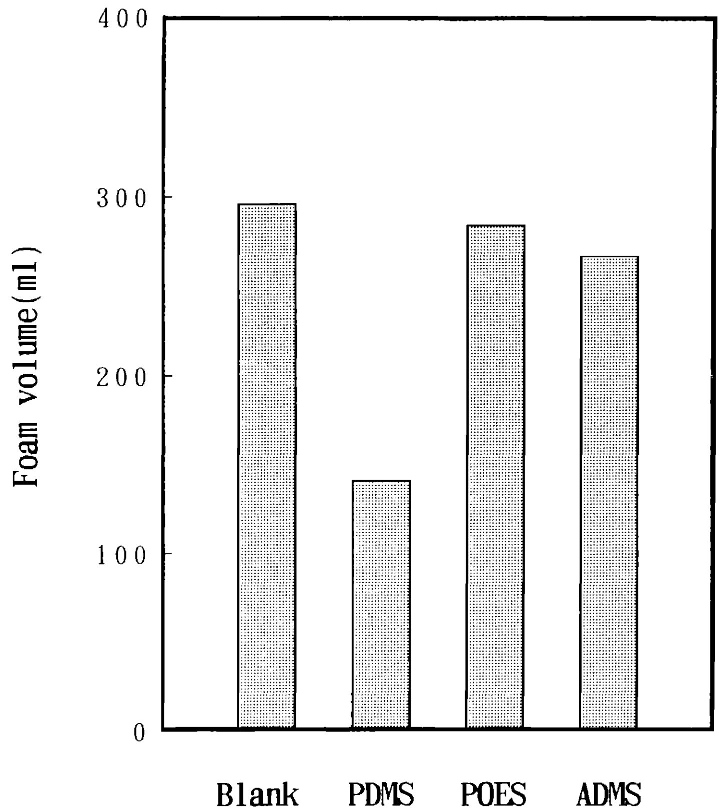


Figure 8. Changes in the foam volume of model shampoos containing 2 wt% silicones. Each shampoo was diluted with 40°C, 4° DH water to prepare a 0.5% shampoo solution containing 0.3 wt% model sebum.

stable vapor–liquid interface resulting from the formation of PDMS thin films at the water surface. In the case of POES and ADMS systems, on the other hand, these silicones had little effect on the foam volume.

Figure 9 shows the measurement of dynamic combing force (DCF) through the shampoo and drying process. This experiment was performed on tufts of hair to which the model "2 in 1" shampoos were applied. For dry conditions, PDMS with high molecular weight was the most effective compared with the other silicones, and this silicone made hair light and extra smooth to the touch. POES with low HLB, which forms liquid crystal in water, were specially effective in reducing combing force while the hair was in contact with running water. By the application of ADMS, which were selectively adsorbed on damaged sites of the hair surface, altering hair surface properties to more hydrophobic conditions, the combing force was retained at a low level throughout the drying process. Consequently, ADMS make hair naturally manageable, eliminating the necessity of blow drying, and they effectively control flyaway of hair tips.

In conclusion, use of silicones has enabled formulation of new types of conditioning or "2 in 1" shampoos, and the selection and combination of silicones is of special importance.

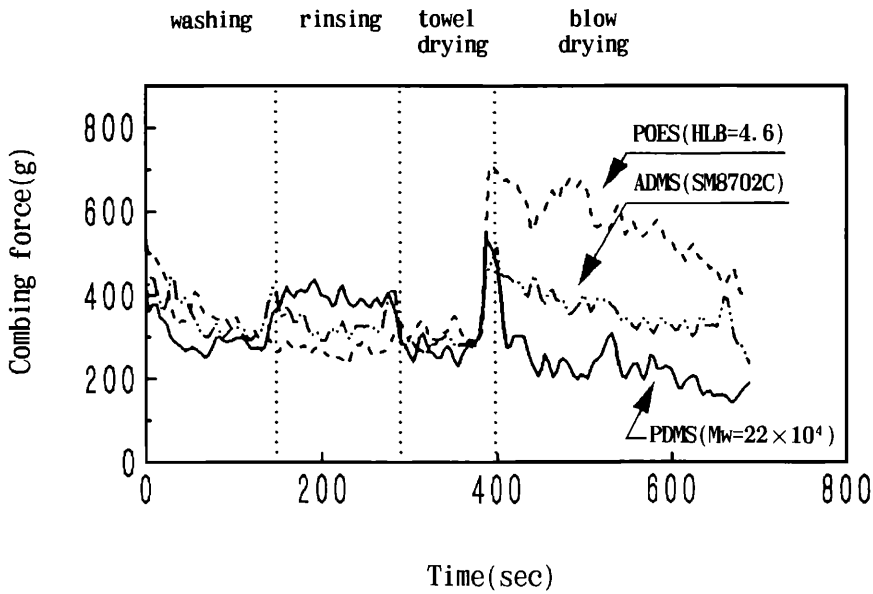


Figure 9. Dynamic combing force during shampooing process as a function of time.

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