The feature of Microcapsule Involving Ultraviolet Rays Absorbent

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Summary

A new method was developed to prepare microcapsules involving hydrophobic components. A totally new "silicone-resin-polypeptide" was used as the wall materials. The polypeptide was made by hydrolysis of collagen and silk protein and so on, and that was combined with silicone. This microcapsule was easily prepared from silicone-resin-polypeptide in water solution. The ratio of encapsulation in the microcapsule was not only high level as 90%, which had never been reached, but also the particle size could be controlled to obtain very small size (average particle size: 2μm). Moreover, these microcapsules were resistant to high shearing forces and were stable over a long time period. This stable microcapsule was not crushed in pressure with finger spreading, so the core materials hardly touch the skin directly.

Application in cosmetics by using microcapsule involving UV absorbents (2-ethylhexyl-4-methoxycinnamate (OMC) and 4-tert-butyl-4'-methoxydibenzoyl-methane (BMDBM)) was examined. It was possible to apply organic UV absorbents in water-rich formulations without any surfactant by using this microcapsule. This formulation demonstrated a good moisturizing and soft skin feel. Therefore, the microcapsule was applied to hair care products. As a result, the sunscreen hair lotion with microcapsule was able to prevent from damaging and decoloring of hair color by UV rays. As just, it was suggested that this microcapsules were be widely applied in cosmetics.

Introduction

Many studies on the preparation and application of microcapsules have been reported previously [1-6]. In general, polymers such as gelatin, polysaccharides and polyvinyl alcohol have been used as wall material of microcapsule [7]. We developed a novel encapsulation technology by using silicone-resin-polypeptide as entirely wall material. This silicone-resin-polypeptide consists the polypeptide part and the silicone resin part. The former functions as a hydrophilic group, whereas the latter acts as hydrophobic group. This microcapsule was prepared due to using emulsificated polymerization method. The UV absorbents were used as encapsulated material in

microcapsule. The UV absorbents are important cosmetics ingredients that protect the skin from sunburn by UV rays. However, some UV absorbents have some problems such as skin irritation [8], oily feeling, its particular odor and its poor compatibility with cosmetics ingredients [9]. Therefore, preparing the microcapsule involving UV absorbents was examined for these problems, and we studied on developing new cosmetics items by using microcapsulating technology. Moreover, the microcapsule allows to be applied for not only skin care products but also hair care products, because the hair was influenced by UV radiation [10-12].

Methods

Preparation of microcapsule

UV absorbents were added to aqueous solution of the silicone-resin-polypeptide and homogenized. The condensation reaction of the silicone was occurred automatically on the oil and water interface by changing the preparation conditions (e.g., pH, temperature, reaction time) and microcapsule water dispersion was obtained.

Measurement of physical properties

SEM observation

Microcapsule water dispersion was frozen, and freeze-dried stepwise under low and high vacuum during 20 minutes each. The samples were observed with scanning electron microscope (JSM-5800LV; JEOL Co., Ltd.).

Optical microscope observation

Microcapsule water dispersion of average particle size 10 μm was prepared and placed between a slide glass and cover slip, and pushed down to destroy the microcapsule. The destroyed microcapsules were observed with optical microscope (BHSP; Olympus Optics Co., Ltd.).

Laser microscope observation

The microcapsule water dispersion was uniformly spread on the skin of a Yucatan piglet (Japanese Charles River Laboratories). The condition and the stability was observed with Color laser 3D profile microscope (VK-8500;Keyence Co., Ltd.).

Determination of the total amount of UV absorbent

0.05 g of microcapsule water dispersion was weighed, put into a measuring flask, filled up with ethyl-acetate, and sonified for 30 minutes to extract the UV absorbents. The ethyl-acetate solution was passed through a filter to remove the wall material. And the quantity of the UV absorbents were measured by HPLC on the condition, ODS-120T ϕ4.6\150 (TOSO Co., Ltd.), water-methanol (5:95) 0.8 mL/minute. The OMC was detected at 308 nm and the BMDBM was detected at 358 nm.

Determination of the total amount of non-encapsulated UV absorbent

The following method was estimated to confirm the amount of non-encapsulated UV

absorbents outside of microcapsule.

0.1 g of microcapsule water dispersion was put into sample glass bottle (φ27×55(mm)) and 4.9 g of purified water was added. 10mL of isopropyl myristate (IPM) was added and rotated with shaker at 150 rpm (Figure 1). This extraction with IPM was continued for 2 and 8 minutes. The extracted IPM solutions were passed thorough a filter. The filtrate was diluted with n-hexane, and the quantity of the UV absorbents were measured by HPLC on the above condition.

INSERT FIGURE 1

Calculation of the amount of encapsulated UV absorbent

The amount of encapsulated UV absorbent in the microcapsule water dispersion can be calculated from the following formula.

(Encapsulated UV absorbent content)
= (Total UV absorbent content) – (Non-encapsulated UV absorbent content)

The graph of Figure 2 shows the relationship between the extracted concentration of UV absorbents in the IPM layer and the extraction time. From this results, the line $Y = aX + b$ could be obtained. The slope a stands at the elution rate, and intercept b for the concentration of non-encapsulated UV absorbents, and X for the elution time

INSERT FIGURE 2

Particle size distribution

The particle size distribution of the microcapsule water dispersion was measured with a Laser diffraction particle size analyzer (SALD-2100; Shimadzu Co., Ltd.).

Resistance against shearing force

Microcapsule water dispersion was stirred for 30 minutes at 20 to 25 °C using a T.K. auto homo-mixer (MARK II 2.5; Tokushu Kika Kogyo Co., Ltd.). Thereafter, the concentration of encapsulated UV absorbents in this dispersion was measured as described above. The change in the encapsulated UV absorbents concentration was taken as a measure for the stability of the microcapsule under shear.

Long term stability

15 g of microcapsule water dispersion was put into sample glass bottle (φ27×55(mm)), sealed and shielded from sun light. Subsequently, the sample bottles were placed at 20°C, 40 °C, and between 5 °C and 40 °C (oscillating at a two days cycle) for 180 days. Thereafter, the amount of encapsulated UV absorbents in this dispersion were measured as described above. The change in the concentration of encapsulated UV absorbents was taken as measure for the stability of the microcapsule.

Penetration test

Each formulation was applied to forearm of three Japanese volunteers (Table I). This test was performed according to "tape-stripping method" [13].

INSERT TABLE I

Viscosity stability test of carbomer under UV rays

The gel samples were prepared (Table II). The each sample was put in the glass bottle and the bottles were fallen sideways. UV irradiater (SPECTROLINE LONGLIFE FILTER ENB-280C/J (SPECTRONICS) was set the side of the bottles. The bottles were exposured by UV light at 312 nm for 96 hours. Every sixteen hours, the viscosity was measured by BROOKFIELD Viscometer (BROOKFIELD ENGINEERING LABORATORIES).

INSERT TABLE II

Application for cosmetics (skin-care formulation)

Study on no surfactant formulation

One of the advantages of microcapsules is their excellent dispersibility in water. It was studied whether milky lotions of these microparticles could be formulated without any surfactants (Table III). In addition, the textures of formulations that were with and without microcapsule were evaluated.

INSERT TABLE III

Application for cosmetics (hair-care formulation)

Any hairs that were applied for this study were collected from a unique Japanese female. And these have never been treated with chemicals. The extremely thinner or thicker hairs were eliminated by visual criteria. The tresses were made to be 1 g in weight and 10 cm in. Each tress was soaked with 2 % sodium POE(3) lauryl ether sulfate aqueous solution at 40°C for 30 minutes. After that, the soaked tresses were rinsed with tap water and dried by hair dryer.

A tress was bleached with 1:1 (w/w) mixture solution of 6% hydrogen peroxide and 2% ammonium hydroxide for 30 minutes, then rinsed with tap water. The tress was transferred in a buffer solution that was prepared as pH 3 with 0.1 M citric acid and 0.2 M disodium hydrogen phosphate for 5 minutes, then rinsed with tap water and dried by hair dryer. This process was repeated 5 times.

Commercial hair dye was applied to the above bleached tress. The ratio of dye and the tress was 1:1 (w/w). Then the tress was incubated at 40°C for 30 minutes, then rinsed with tap water for 30 seconds and dried by hair dryer.

Tresses were treated with sunscreen hair lotion (Table IV). And they were exposed to sunlight for leaving at outside for 6 hours (9:00-15:00), and treated with shampoo. This procedure was repeated for 10 or 20 days. The tresses treated for 10 days were observed with scanning electron microscope (SEM) and laser microscope. The tresses treated for 20 days were tested with high sensitivity hair rheology analyzer.

INSERT TABLE IV

SEM observation

Surface condition of hair was observed with scanning electron microscope.
A hair was knotted and hung with 1 g of weight at the bottom end of the hair for 20 seconds. Observation was carried out in mainly curved area of the knot.

Laser microscopic observation

Observation of decoloring intensity [14] was evaluated with Color laser 3D profile microscope. The photo image obtained with the laser microscope was divided into 786432 pixels, and color data in RGB index was measured on each pixel. The obtained color data in RGB index of each pixel was shown in 256 gradation of brightness. The 49152 pixels color data in RGB index was extracted evenly from original 786432 pixels data. The color data was compared to each average value of hair surface.

Tensile strength

Tensile strength of hair was measured by a high sensitivity hair rheology analyzer (model: KES-G1-SH, KATO TECH CO., Ltd.) at breaking strength, when a hair was torn off. The gauge length was 50 mm with a 0.5 mm/sec.

Results and Discussion

Preparation of microcapsule water dispersion

Two samples were able to prepare. Sample A was a 60% water dispersion of OMC-containing microcapsules and a sample B was a 60% water dispersion of OMC/BMDBM mixture-containing microcapsules.

Measurement of physical properties

SEM observation

SEM photographs of sample B were obtained (Figure 3), the globular and smooth nature microcapsules were observed.

INSERT FIGURE 3

Optical microscope observation

The 10μm diameter of microcapsule was destroyed with stress (Figure 4). The encapsulated oil was released from the capsule. This fact showed that the microcapsule was consisted of encapsulated material and wall material.

INSERT FIGURE 4

Laser microscope observation

The microcapsules could be observed on the skin surface as these photographs (Figure 5). The spreaded microcapsules maintained their original form on the skin, probably because the average particle size was too small to be broken by the pressure with a finger. It was therefore concluded that most of the encapsulated UV absorbent was not contact immediately to the skin.

INSERT FIGURE 5

Determination of the amount of non-encapsulated UV absorbent

The results of the extraction test carried out on sample B were shown in Table V. From the linear function that could be derived from this extraction test, the elution rate of OMC / BMDBM (%/minute), and the concentration of non-encapsulated UV absorbent content could be derived from the slop and the intercept. This extraction test method was also used for the evaluation of the stability of the microcapsules.

INSERT TABLE V

Measurement of particle size distribution

It was possible to create any particle size of microcapsules with a uniform distribution of a smaller (average particle diameter was 2.2μm) and a larger particle size (average particle diameter was 11.5μm) (Figure 6). Any particle size of microcapsule could be obtained if condition of the preparation was changed.

INSERT FIGURE 6

Resistance test to shearing force

The encapsulated OMC concentration was constant for comparing the concentrations prior to mixing and after mixing at 5,000 and 10,000 rpm (Figure 7). This result was demonstrating the stability of microcapsule water dispersion against the shear.

INSERT FIGURE 7

Long term stability

Sample B was exposed to different temperatures. The qualities were measured as the process of time. The change in the concentration of encapsulated OMC extracted from sample B was very small for 180 days (Figure 8). Moreover, there was no change in the particle size distribution of sample B after for 180 days (Figure 9).

These results were demonstrating the stability of microcapsule water dispersion against temperature for long term.

INSERT FIGURE 8 and 9

Penetration test

The ratio of penetrated OMC in the stratum corneum were shown in Table VI. In the case of using sample 1 formulation, about 40 % of OMC was penetrated in the stratum corneum. However, only less than 6.2 % of OMC was penetrated in the sample 2 formulation. The penetration of OMC to the stratum corneum could be significantly decreased.

INSERT TABLE VI

Viscosity stability test of carbomer under UV irradiation

The results of the viscosity carried out on gel samples (Table II) are shown in Figure 10.

The following each result deserves average value in triplicate. The viscosity drop of carbomer gel due to rays was able to be prevented by using microcapsule.

INSERT FIGURE 10

Application for cosmetics (skin-care formulation)

Study on formulation

A water-based sprayable sunscreen could be formulate without any surfactants (Figure 11(No.1)). Cream could also be formulated with sample B (Figure 11(No.2)). These formulations demonstrated a watery texture without any stickiness or oil when applied to skin.

This result was derived from that the oily UV absorbent is encapsulated in the microparticles in these formulations.

INSERT FIGURE 11

Application for cosmetics (hair-care formulation)

Observation of hair exposed to sunlight

The hair surfaces observed with SEM were shown in Figure12. After sunlight exposure, the cuticle cells of the treated sunscreen hair lotion were not lifted up less than the without lotion.

It was suggested that the sunscreen hair lotion protected the hair against the damage of sunlight.

INSERT FIGURE 12

Evaluation of decoloring intensity

The three primary [Red, Green, Blue] reflections light of hair were observed with the laser microscope. The results were shown in Figure13. After sunlight exposure, the color change of the hair treated with sunscreen hair lotion is smaller than that of the without lotion. Both red of them showed a positive correlation with student t-test ($p<0.05$).

As a result, it was suggested that the sunscreen hair lotion protected the hair from decoloring of the hair.

INSERT FIGURE 13

Evaluation of tensile strength

Evaluation of the hair tensile strength, treated or non-treated with sunscreen hair lotion was shown in Figure14. After sunlight exposure, the tensile strength of the treated hair with sunscreen hair lotion kept similar strength to before sunlight exposure. There was the positive correlation with student t-test ($p<0.01$) between before sunlight exposure and without lotion.

It was suggested that the sunscreen hair lotion protected the hair from the strength down.

INSERT FIGURE 14

Conclusions

Microencapsulation using a new silicone-resin-polypeptide as the encapsulating material was studied using UV absorbents as the encapsulated agents. Microencapsulation could be confirmed by SEM and encapsulating efficacies as high as 90% could be achieved. The particle size could be controlled by changing the preparation conditions and microcapsules with diameters as small as 2μm could be prepared. The microcapsule water dispersion was stable against shear force induced by a homogenizer.

Formulations containing these water dispersions were applied to Yucatan pigskin. It could be shown that most of the encapsulated UV absorbent was not direct contact to the skin, because the microcapsules did not break during rubbing of the formulation into the skin. Lotions containing

UV absorbents without surfactants were prepared using the above microcapsules and demonstrated a good feel. Therefore, the sunscreen hair lotion with microcapsule was able to prevent from damaging and decoloring of hair color by UV rays.

Acknowledgment

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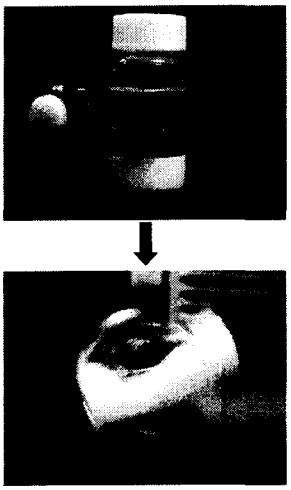


Figure 1: Extraction method

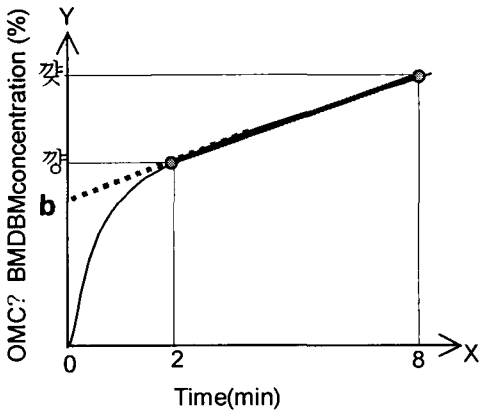
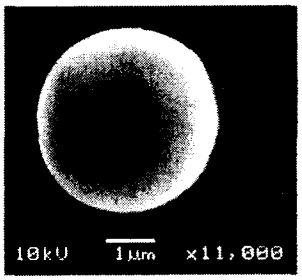


Figure 2: Time course of the concentration of UV absorbent in IPM



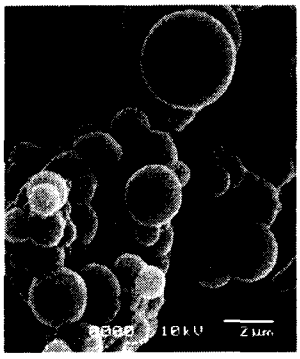


Figure 3: SEM photographs of microcapsule

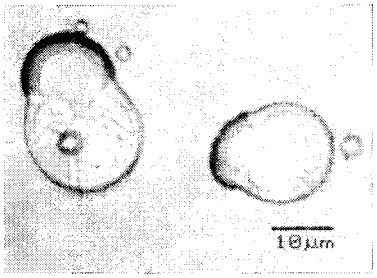


Figure 4: The observation of destroyed microcapsule

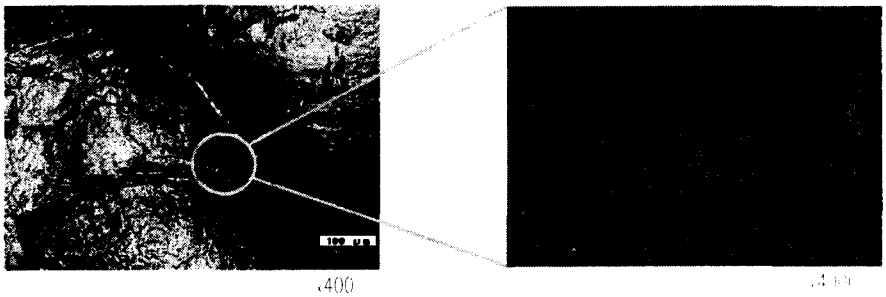


Figure 5: Laser microscope observation of the microcapsule on skin surface (Sample B)

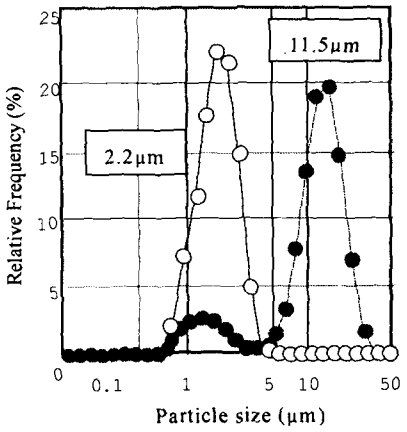


Figure 6: Particle size distribution of microcapsule

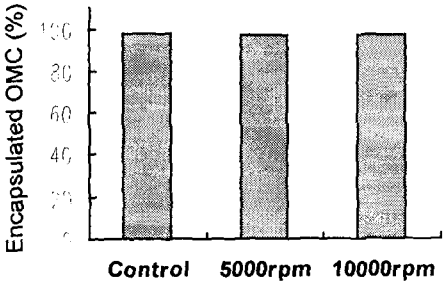


Figure 7: Result of stability against shearing force

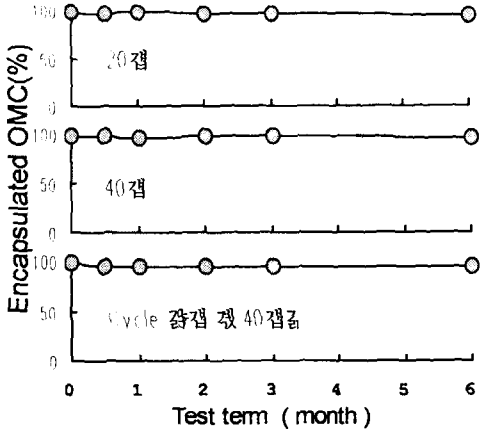


Figure 8: Stability of encapsulation ratio against temperature

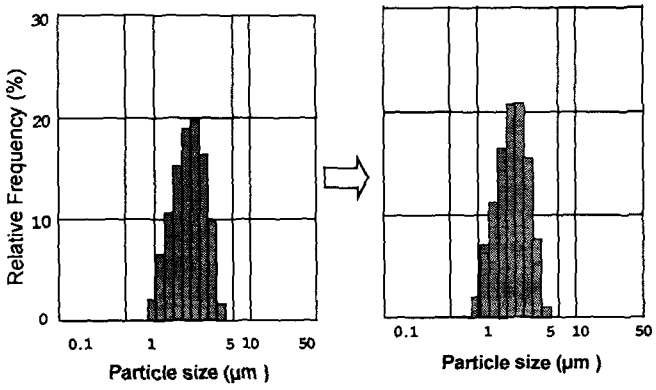


Figure 9: Distribution of microcapsule particle size against temperature

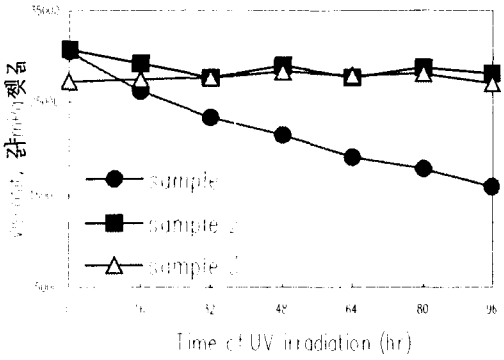


Figure 10: Variation in viscosity of carbomer gel under UV irradiation

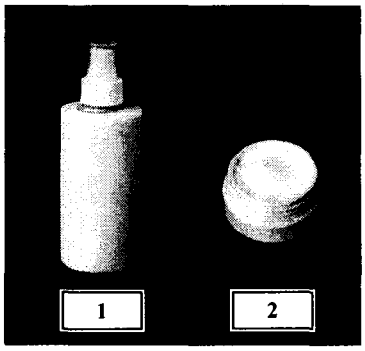


Figure 11: Sunscreen form

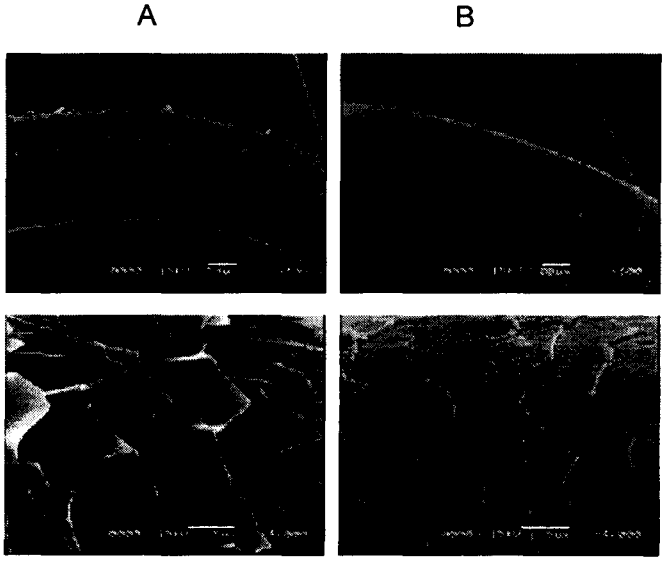


Figure12: SEM photographs of the surface condition of the hair after sunlight exposure.

A; Without lotion B; With lotion

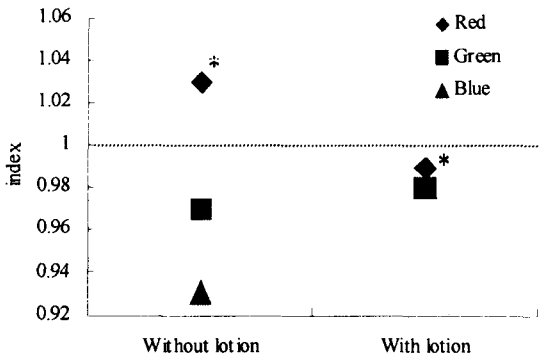


Figure 13: The comparison of average brightness value of hair surface

*: $p<0.05$ n=10

$$\text{Index} = \frac{\text{Color date value of after sunlight exposure (without or with lotion)}}{\text{Color date value of before sunlight exposure}}$$

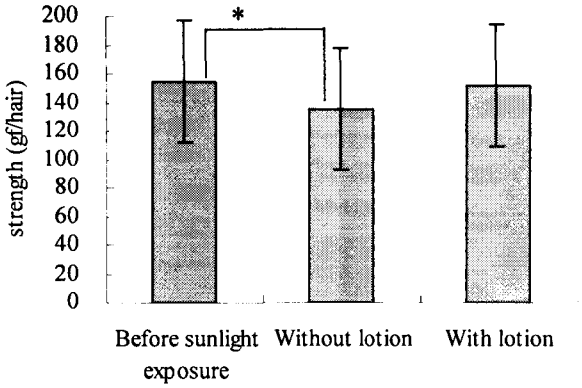


Figure 14: Variation of tensile strength of sunlight exposed hairs n=20 *:p<0.01

Table I: Test formulation sample

	Formulation sample (W%)	
	1	2
Cellulose Gum	1.0	1.0
Sample B	10.0	0.0
OMC	0.0	4.3
Ceteth-25	0.0	1.5
Glycerin	10.0	10.0
Water	79.0	83.2

Table II: Gel sample

	Gel sample (W%)		
	1	2	3
Carbomer	1.0	1.0	1.0
NaOH (10% soln.)	2.3	2.3	2.3
Sample B	0.0	0.1	0.5
Water	96.7	96.6	96.2

Table III: Sunscreen formulation

	Formulation (W%)	
	No.1	No.2
Water (deionized)	83.7	78.7
Sample B	10.0	10.0
Emulsifier*	–	5.0
Ethanol	6.0	6.0
Preservative	0.3	0.3

Emulsifier* (SIMULGEL NS, SEPPIC)

Table IV: Sunscreen hair lotion

Sample B	20.0
Chelating agent	0.3
Titanium dioxide	1.0
Etanol	6.0
Phenoxyethanol	0.3
Water	73.4

(W%)

Table V: Determination of the non-encapsulated UV absorbent content

UV absorbent	Extracted conc. (%)		Elution rate (%/min.)	Non-encapsulated conc. (%)
	2 min.	8 min.		
OMC	0.643	0.995	0.061	0.494
BMDBM	0.072	0.126	0.009	0.054

Table VI: OMC penetration in the stratum corneum

Volunteer	Distribution ratio (%)	
	Sample 1*	Sample 2*
1	42.9	3.5
2	26.0	6.2
3	39.6	3.6

*:$p<0.05$ n=3