Development of newly multifunction cosmetic raw materials and its applications

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SUMMARY

Moisturizing the skin is one of the most important functions of skincare cosmetics, because water plays a significant role in keeping the skin healthy. There are various humectants including polyol (glycerin and 1,3-butylene glycol), water-soluble polymers, and botanical extracts. It is well known that the increased amount of polyol in lotion for obtaining high moisturizing effect gives a sticky feeling to the skin. Therefore, a few humectants that can give high moisturizing effect without a sticky feeling for lotion formula is available. On the other hand, oil-based lipstick is well known to have a difficulty to contain a large amount of hydrophilic humectants, because the humectants is unable to be mixed well into oil-based lipsticks and give the lips a peculiar taste.

There are newly developed humectants, polyoxyethylene/polyoxypropylene dimethyl ether (EPDME) that can solve these problems describable above. EPDME is a random copolymer of ethylene oxide and propylene oxide. EPDME gives a low sticky feeling with a high moisturizing effect when it is used in lotion. As a remarkable character, EPDME can show not only a preventing effect on rough and dry skin, but also a improving effect upon the use for 1-4 weeks. EPDME can show a synergistic effect with glycerin on preventing to rough and dry skin. Since EPDME can be dissolved in oil-based formulation and used as an ingredient of lipsticks, EPDME can give a moisturizing effect that allows lip to be healthy condition. EPDME can also give no peculiar taste even upon the use of a large amount. EPDME is a useful cosmetic ingredient that can show a good skin care effect in both water-based formula and oil-based formula. EPDME of which polarity can be controllable is expected to be used for various cosmetic applications in near future.

1. INTRODUCTION

Moisturizing is closely related to the preservation of good skin condition. And NMF (natural moisturizing factor) has an important role in the healthy skin. For this reason, moisturizing skin is one of the major expected functions of cosmetics. Humectants usually used in cosmetics are polyols (glycerin and 1,3-butylene glycol), water-soluble polymers (hyaluronic acid, etc.) and botanical extracts. [1] However, when polyols (the most frequently used in aqueous-base component in lotions) is added to cosmetic formula for increasing its moisture-retaining effects, the resultant cosmetics have problems such as a sticky feeling. Thus, very few materials currently available satisfy both requirements, ease in handling and high moisture-retaining effect.

The lip is particularly likely to become rough and dry [2], since the stratum corneum of the lip is thinner than that of the other part of the skin, and the amount of other physiological components such as NMF is lower than that of other part of skin [3]. Various lip creams and lipsticks have been developed to solve this problem. In recent years, lip creams and lipsticks that contain emulsified water or humectants to exert moisture-retaining effects [4] and those containing highly water-holding emollient [5-7] have been launched on the market. Despite these products available on the market, there are still many people who suffer from lip drying. It has been desired to develop lipstick bases, which have an excellent moisture-retaining effect. Since lipsticks are oily bases, it is difficult to add hydrophilic moisture-retaining components in large amounts due to their low compatibility with oily components, etc. Furthermore, since many humectants have their specific taste, the taste becomes a problem if such agents are added in large amounts to lipsticks.

We recently found that dimethylether of random copolymer of ethylene oxide and propylene oxide (EPDME) can dissolve the problems described above.

This paper presents the characteristics of EPDME, which exert excellent skin-caring effects (moisture retention, prevention and improvement of dry skin, etc.) when it is added to not only aqueous but also oily bases.

2. Materials and Methods

2-1. Materials

Figure 1 shows the basic structure of EPDME used in this study. The m/n ratio is variable. EPDME (14/7), shown as (a) of Figure 1, was used for aqueous bases. EPDME (36/41), shown as (b), was used for oily bases. Both were synthesized and purified before added to base. In addition, a commercially available glycerin (Sakamoto Yakuhin Kogyo, Osaka, Japan), 1,3-butylene glycol (Daicel Chemical Industries, Osaka), 2-cetyl ethylhexanoate (Nikko Chemicals, Tokyo), and polyethylene glycol 400 (Sanyo Chemical Industries, Kyoto) were used without further purification.

$$CH_3O\text{-}(CH_2CH_2O)m/(\underset{\displaystyle CH_3}{C}HCH_2O)n\text{-}CH_3$$

Figure 1 Molecular structure of polyoxyethylene/polyoxypropylene dimethyl ether (EPDME). Two EPDME were used in this study, (a) EPDME(14/7) and (b) EPDME(36/41). EPDME (m/n), where m and n represent the average molecular ratio of ethylene oxide and propylene oxide, respectively. EPDME is a random copolymer of ethylene and propylene oxide.

2-2. Evaluation of solubility

The solubility of EPDME (14/7) and EPDME (36/41) in various solvents was examined and compared with glycerin. At 24 °C, each sample was added in concentrations of 1%, 30%, and 50% to various solvents, and the solubility was evaluated 1 hr later by naked eye.

2-3. Measurement of the equilibrium moisture content of EPDME

At 24 °C and a relative humidity (RH) of 92%, EPDME (14/7), EPDME (36/41), glycerin (a humectant), and 2-cetyl ethylhexanoate (an oily component) were left standing until equilibrium (196 hr). The moisture absorption rate (molar percentage of water contained in each sample) was calculated using the following equation:

Moisture absorption rate (mol %) = [Mol. no. of absorbed water / (mol. no. of sample + mol. no. of absorbed water) x 100]

2-4. Evaluation of sticky feeling by rolling friction measurement

The adhesive property of EPDME (14/7), glycerin, polyethylene glycol 400 (mol. wt.: 400), and 1,3-butylene glycol were evaluated by a modified friction tester equipped with a roller probe [8]. At 25 °C and 50% RH, each sample (10μL) was dropped onto the tester, and the 5-min mean friction was measured.

2-5. Evaluation of moisture retention property

The moisture retaining property of sample was evaluated by 8 healthy volunteers. The inner forearm of panels was washed with soap, followed by the application of 10% aqueous solution of each sample (the final dose: 2μL/cm^2) at 24 °C and 46%RH. Two hours later, the moisture content in the stratum corneum of the sample-applied area was measured by a stratum corneum hydrometer, Corneometer CM825 (C+K Electric, Köln, Germany).

2-6. Efficacy of EPDME for experimental dry skin

For evaluating the effect of the test substance on the dry skin induced artificially with sodium dodecyl sulfate (SDS), 100μL of 5% SDS was applied to the inner forearm of healthy volunteer (n = 9) for 10 min. The applied site was washed with water, and then the sample was applied in appropriate amounts. This treatment was repeated for 5 days. On the 6th day, the sample-applied area was washed with soap, and the physiological parameters of skin were evaluated 20 min later. The water content of stratum corneum was measured by Corneometer CM825. The trans-epidermal water loss (TEWL) was measured by a special instrument for TEWL, Tewameter TM210 (C+K Electronic).

2-7. Measurement of glycerin permeation through the stratum corneum

The inner forearm of healthy volunteer (n = 4) was washed with soap. Then, either 10% glycerin or 10% glycerin with 5% EPDME (14/7) was applied to the skin (the final dose: 1 mL/cm^2). Four hours later, the solution-applied area was washed, and the stratum corneum was collected by tape stripping procedure. Glycerin was extracted with 10 mL water, and the amount of the glycerin was measured by HPLC with a pulse type electrochemical detector, Nanospace Pulsed Amperometric Detector 3016 (Shiseido, Tokyo).

2-8. Confirmation of the efficacy of lotion contain EPDME in winter

Males with dry skin (n = 20) in winter (March to April 2002 in Yokohama) used a lotion containing 3% EPDME (14/7) with 7% glycerin or a lotion containing 7% glycerin once or more times a day (in morning and/or evening) for 4 weeks. Each panel applied one of these two cosmetics to the half of his face and the other cosmetic to the other half of his face. Four weeks later, the water content in the stratum corneum and TEWL were measured at 24 °C and 46% RH by Corneometer CM825 and Tewameter TM210, respectively. The skin surface morphology was evaluated by two-dimensional image analysis of the skin replica prepared with silicone rubber. As parameters of skin texture, the anisotropy of skin furrows (VC1) and the average of skin roughness (KSD) were evaluated [9]. During the test period, panels were unable to be allowed to use any other cosmetics to their face.

2-9. Evaluation of lip moisture retention

At 25 °C with 50%RH, the lip of healthy volunteers (n = 8) was washed with water, and then a lipstick containing with and without 5% EPDME (36/41) were applied to the left and the right half of the lip, respectively. Two hours later, the lipstick was wiped off by tissue papers from the lip, and the conductance was measured with a stratum corneum hydrometer, SKICON-200 (IBS, Shizuoka, Japan).

2-10. Confirmation of the efficacy of EPDME for lip

Ten females with dry lip skin used a lipstick containing with and without 5% EPDME (36/41) lipstick three times a day for 2 weeks (June 2002 in Yokohama). Then, the improvement of dryness of the lips was evaluated through measuring the moisture content in a stratum corneum by SKICON-200 and photographs.

3. Result

3-1. Evaluation of solubility

Glycerin, which serves as a standard humectant, is soluble in water and insoluble in oil. On the other hand, EPDME was found to be soluble in both water and oil.

Table 1 Solubility of EPDME(14/7), EPDME(36/41) and glycerin in emollient oils and water.

	EPDME(14/7) (%)			EPDME(36/41) (%)			Glycerin (%)		
Solvent	1	30	50	1	3	50	1	30	50
Methylphenyl polysiloxane	S	S	S	S	S	S	I	I	I
Macadamia nut oil	S	S	S	S	S	S	I	I	I
Glyceryl trioctanoate	S	S	S	S	S	S	I	I	I
Water	S	S	S	S	S	I	S	S	S

S : soluble I : insoluble EPDME(14/7), EPDME(36/41), and glycerin were solubilized at 24 갤, then each solition was stood for 1h at 24 갤.

3-2. Measurement of equilibrium moisture content

Figure 2 shows the moisture absorption rate (mol %) of EPDME compared with glycerin or emollient oil. The higher rate indicates that the capacity to retain moisture becomes greater. The oily component 2-cetyl ethylhexanoate showed hardly any moisture-retaining capacity, while EPDME (14/7) and EPDME (36/41) showed a moisture-retaining capacity comparable to that of glycerin.

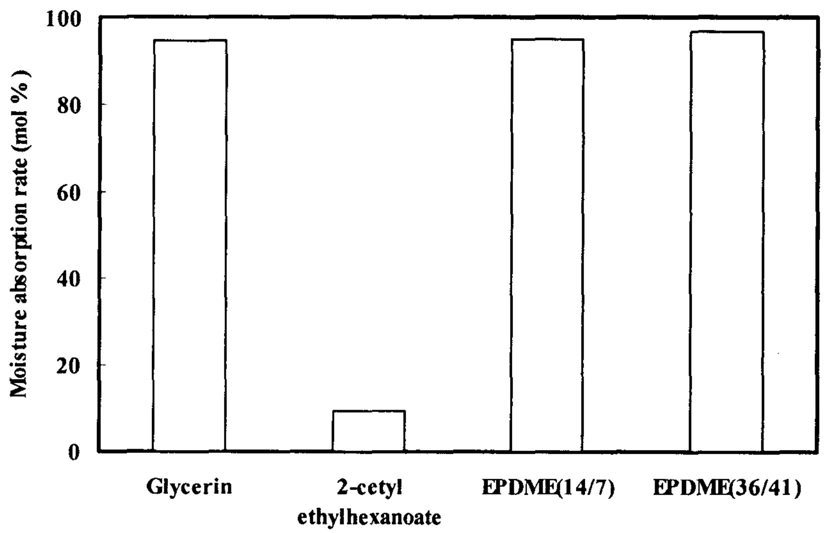


Figure 2 The moisture absorption rate (mol %) of samples.

3-3. Evaluation of sticky feeling by rolling friction measurement

Figure 3 shows the rolling friction data of EPDME compared with the other humectants. It is known that, if the rolling friction of a cosmetic becomes lower, the cosmetic gives less sticky feeling. EPDME (14/7) was significantly less adhesive than glycerin and polyethylene glycol 400. The adhesive property of EPDME (14/7) was comparable to that of 1,3-butylene glycol which is one of the widely used humectants with good texture.

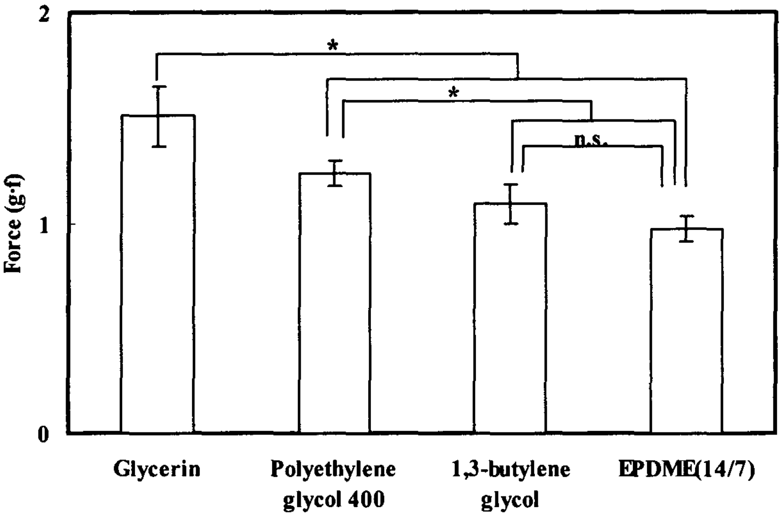


Figure 3 Result of adhesive property of humectants by rolling friction measurement. Data are expressd as mean standard deviation (n = 5).
* : p <0.05, n.s. : not significant (Tukey-Kramer test)

3-4. Evaluation of moisture retention property

Figure 4 shows the moisture content of the stratum corneum. Higher moisture content of the stratum corneum shows higher moisture-retaining effects of the skin. Moisture-retaining effects of the skin were significantly higher in the aqueous EPDME (14/7) solution applied group than in the aqueous 1,3-butyle glycol solution applied group. The moisture-retaining effect of the skin in the aqueous EPDME (14/7) solution applied group was comparable to that in the group in which aqueous glycerin solution (known to have high moisture-retaining effects of the skin) was applied.

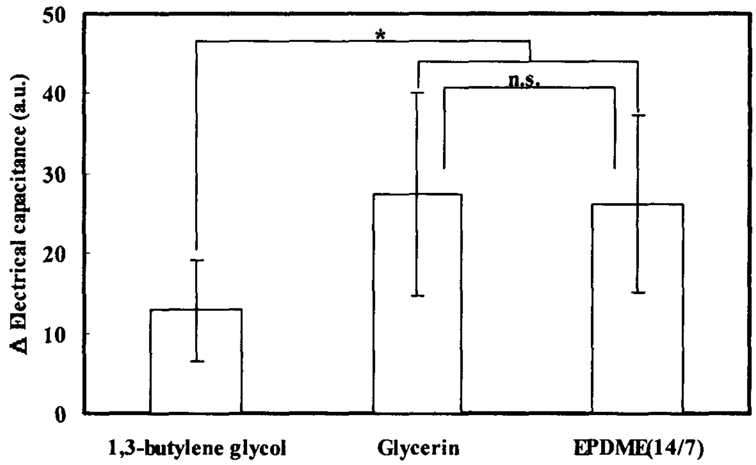
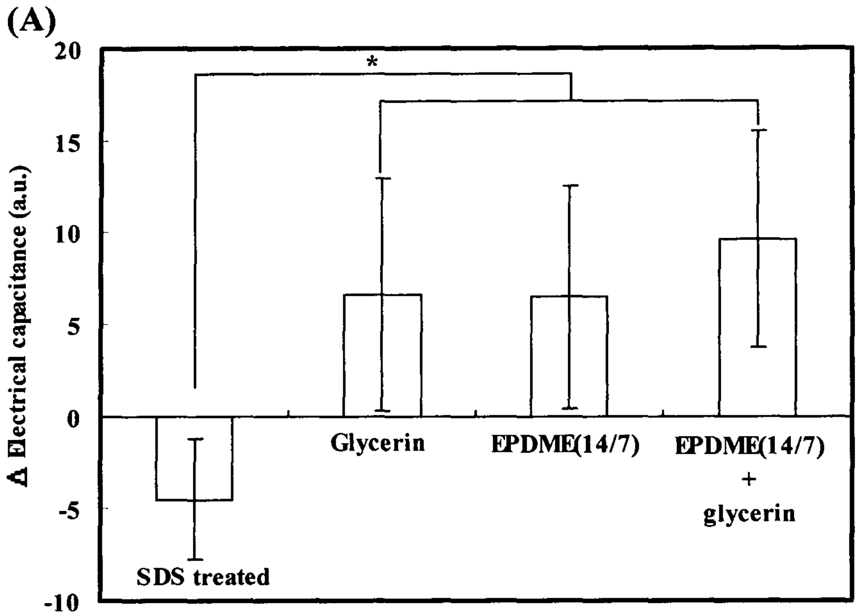


Figure 4 Evaluation of moisuture retension property. Data are expressed as mean ± standard deviation (n = 8). * : p<0.05, n.s. : not significant (Turkey-Kramer test)

3-5. Efficacy of EPDME for experimental dry skin

Figure 5(A) shows the efficacy of EPDME for experimentally induced dry skin by evaluating the moisture contents of the stratum corneum. Greater moisture contents show more effective prevention of skin drying. Comparing with the SDS-treated skin areas (the control), the skin areas treated with EPDME (14/7) showed significantly high moisture contents in the stratum corneum, indicating that EPDME (14/7) prevented the SDS-induced experimental skin drying. It was also demonstrated that the effect in preventing skin drying was enhanced synergistically by applying EPDME (14/7) in combination with glycerin, as compared to the group where either glycerin or EPDME (14/7) was applied,

Figure 5(B) shows the efficacy of EPDME for the experimental dry skin evaluating the TEWL. A low TEWL shows higher barrier function. As compared to the SDS-treated skin area, the areas treated with EPDME (14/7) with or without glycerin showed significantly higher barrier function, suggesting that EPDME (14/7) prevents the SDS-induced experimental damage of the barrier of stratum corneum.



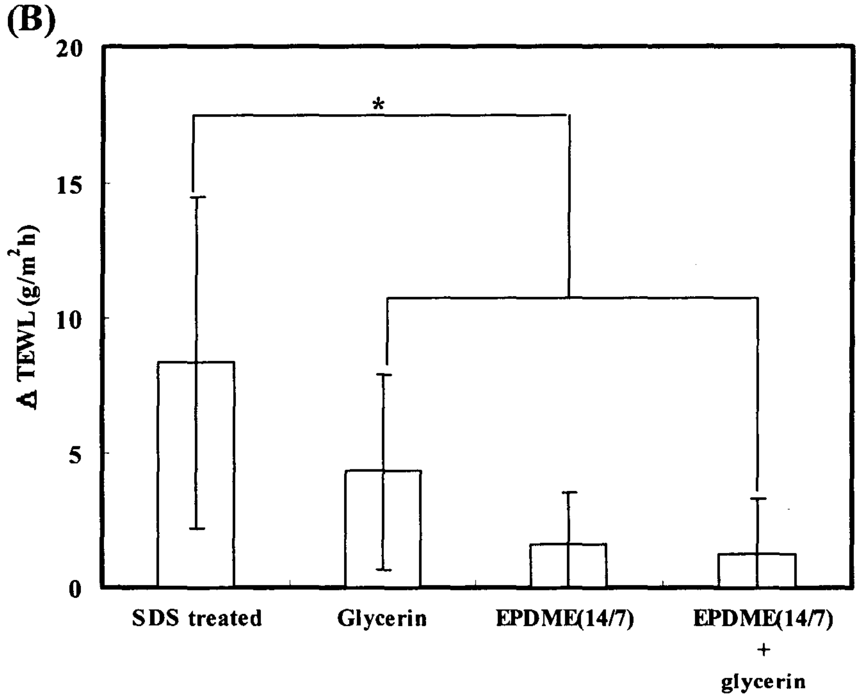


Figure 5 Efficacy of EPDME(14/7) for experimental dry skin. (A) : Moisture contents in starum corneum, (B) : Transepidermal water loss (TEWL). Data are expressed as mean ± standard deviation (n = 9).
* : p<0.05, n.s. : not significant (Turkey-Kramer test)

3-6. Measurement of glycerin permeation through the stratum corneum

Figure 6 shows the quantity of glycerin permeation across the stratum corneum following EPDME (14/7)-glycerin application. The use of glycerin in combination with EPDME (14/7) resulted in approximate 40% increase in glycerin contents in the stratum corneum, as compared to the only glycerin applied group. This result indicates that EPDME (14/7) allows more facilitate the permeation of glycerin across the stratum corneum.

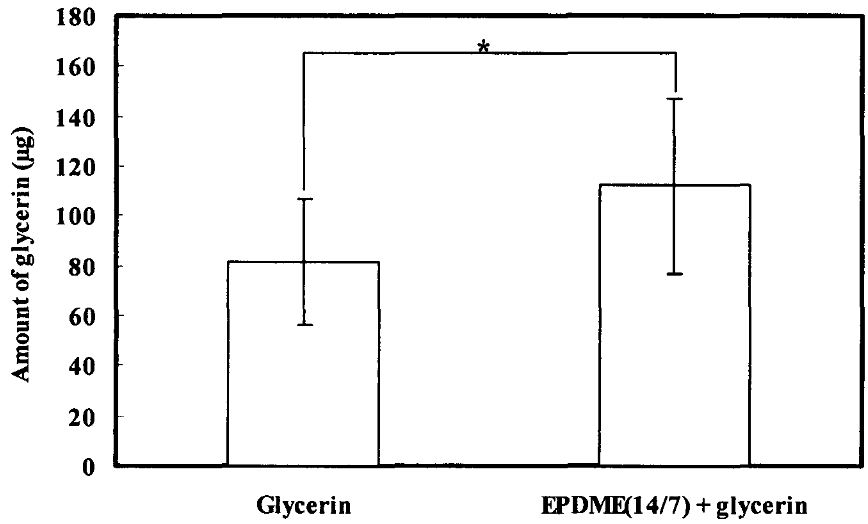


Figure 6 Effect of EPDME(14/7) in the glycerin permeation across the starum corneum. Data are expressed as mean ± standard deviation (n = 4). * : p<0.05 (paired t-test)

3-7. Confirmation of the efficacy of a lotion contain EPDME in winter

Higher moisture contents in the stratum corneum indicate higher improvement of skin drying. Lower TEWL indicates higher barrier-function. Lower VC1 or higher KSD indicates more improvement in the facial skin surface texture

As shown in Table 2, the use of the lotion composed of EPDME (14/7) and glycerin for 4 weeks resulted in significant improvements in the moisture contents of the stratum corneum and TEWL, as compared to their baseline levels before use. The parameter of skin surface morphology improved significantly. These results suggest that the daily use of the lotion composed of EPDME (14/7) and glycerin can significantly improve dry skin.

Table 3 compares the results in the application of the lotion containing EPDME (14/7) with the lotion containing only glycerin. The lotion composed of EPDME (14/7) and glycerin was found to improve moisture contents in the stratum corneum and TEWL significantly more greatly. Although the difference of the change in the facial skin texture of the application of the lotions was very similar, the average of skin roughness (KSD) tended to increase in the EPDME (14/7) with glycerin applied group.

Table 2 Effect of daily use of the lotion EPDME(14/7) with glycerin in improvement dry skin in comparison between the before and after treatment.

	Before treatment	After treatment	
Examination item	Mean ? S.D.	Mean ? S.D.	paired *t*-test
Electrical capacitance	33.76 ? 11.83	44.88 ? 13.27	*
TEWL	23.76 ? 6.29	18.24 ? 4.80	*
VC1	0.508 ? 0.154	0.412 ? 0.106	*
KSD	29.95 ? 6.53	33.94 ? 4.47	*

VC1 : Variation coefficient of number of black dots in each of 13 x 13 meshes composing binary image. KSD : Standard deviation of gray level value at each pixel TV image.
* : $p<0.05$

Table 3 Effect of the lotion EPDME(14/7) with glycerin in improvement dry skin in comparison to those of glycerin.

	Glycerin only group	Containing EPDME(14/7) and glycerin group	
Examination item	Mean ? S.D.	Mean ? S.D.	paired t-test
Δ Electrical capacitance	3.25 ? 10.05	9.86 ? 11.12	*
Δ TEWL	2.64 ? 5.23	-5.54 ? 4.90	*
Δ VC1	-0.0495 ? 0.228	-0.0965 ? 0.146	n.s.
Δ KSD	0.463 ? 8.15	3.988 ? 6.98	+

VC1 : Variation coefficient of number of black dots in each of 13 x 13 meshes composing binary image. KSD : Standard deviation of gray level value at each pixel TV image. Mean value of each parameter indicates the mean difference between the post-treatment and pre-treatment periods.
* : $p<0.05$ + : *p* 긝0.1 n.s. : not significant

3-8. Evaluation of lip moisture retention

Figure 8 shows the moisture contents in the stratum corneum of lips. Higher values of this parameter indicate higher moisture-retaining effects. Lipsticks containing EPDME (36/41) showed to have significantly greater moisture-retaining effects than lipsticks without EPDME.

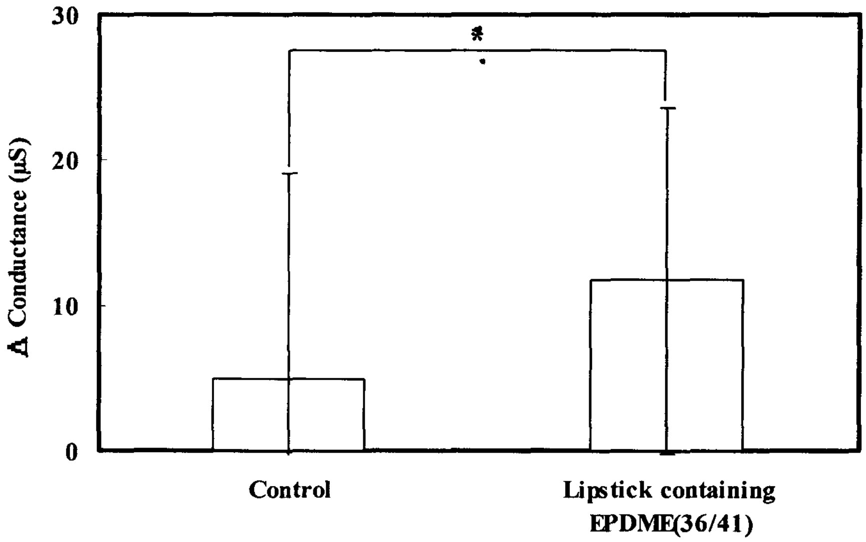


Figure 8 Effect of EPDME(36/41) in lipstick for lip moisturizing.
Data are expressed as mean ± standard deviation (n = 4). * : p<0.05
(paired t- test)

3-9. Confirmation of the efficacy of EPDME for lip in winter

Figure 9 shows the effect of EPDME (36/41) in the change of the moisture contents in the stratum corneum of the lip after two-week daily application. Figure 10 shows the actual photographs of the lip before and after the use of the lipstick. The use of the lipstick containing EPDME (36/41) resulted in higher moisture contents in the stratum corneum. This effect of this lipstick in increasing moisture contents was significantly higher than that of the lipstick without EPDME. The relation was resembled to the relationship shown in Figure 8. The pictures shown in Figure 10 indicate that the dry skin was improved by daily use of this lipstick.

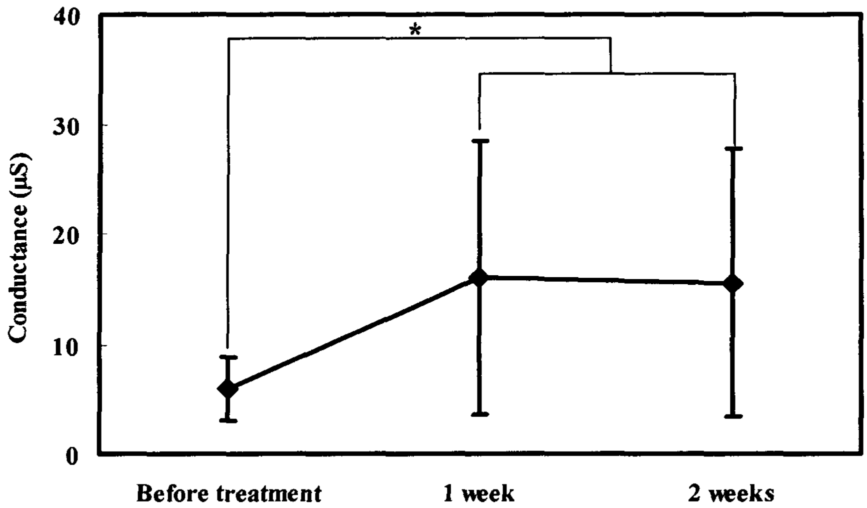


Figure 9 Effect of two-week use of lipsticks containing EPDME(36/41). Data are expressed as mean ± standard deviation (n = 10). * : p<0.05 (paired t-test)

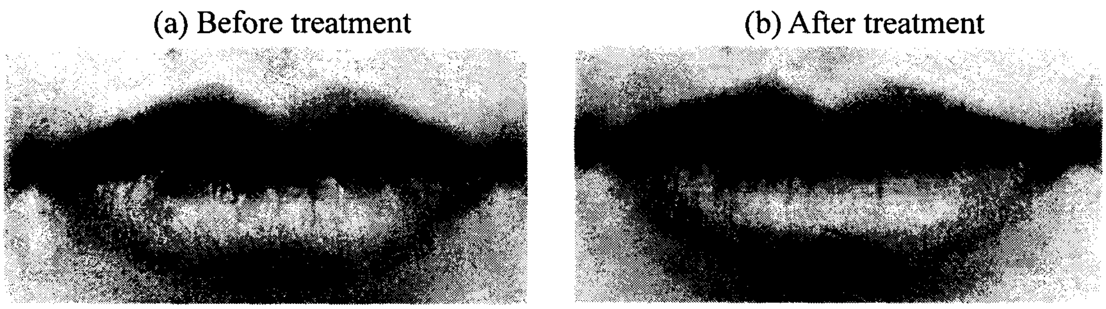


Figure 10 Photographs of before and after treatment by lipstick containing EPDME(36/41)

4. DISCUSSION

It has been difficult to develop cosmetics raw materials that can be handled easily and added to both aqueous and oily bases. When EPDME was used in lotions, it gives less sticky feeling, while it exerted high efficacy to skin (e.g., high moisture-retaining effect, prevention of dry skin, and significant improvement of dry skin by daily application). Furthermore, since EPDME is well soluble with oily components, it can be used in lipsticks, which are composed of oily bases. Lipsticks containing EPDME showed to have high moisture-retaining effects and improved the lips markedly by daily application. Furthermore, unlike conventional humectants, EPDME caused no problem related to taste even when it was added in large amounts. EPDME is composed of random copolymer of ethylene oxide and propylene oxide. Both EPDME (14/7) with a molecular weight of 1,000 and EPDME (36/41) with a molecular weight of 4,000 are a liquid form even at a temperature of $-5\ ^{o}C$ and are thus easy to handle. Regarding solubility in various solvents, Table 1 shows that hydrophilic humectants such as glycerin are insoluble in oil, but that EPDME is highly soluble in both water and oils, since it possesses both hydrophilic and lipophilic groups in its molecular structure. When the solubility in water was compared between EPDME (14/7) and EPDME (36/41), it was possible to prepare a 50% aqueous solution of EPDME (14/7) but impossible to prepare a 50% aqueous solution of EPDME (36/41). This is probably because the lipophilicity of EPDME (36/41) is higher due to the ratio of propylene oxide to ethylene oxide. Regarding the effects of EPDME (14/7), the data on equilibrium moisture content shown in Figure 2 suggest that EPDME (14/7) exerts a high skin moisture-retaining effect comparable to that of glycerin. As shown in Figure 6, the use of glycerin in combination with EPDME (14/7) resulted in about 40% increase of glycerin permeation through the stratum corneum, probably leading to high moisture-retaining effects to the skin. This mechanism seems to explain the significant prevention and improvement of dry skin demonstrated in Figure 5 and Table 2 and 3.

Because glycerin is insoluble in oily components of lipsticks, it is impossible to directly add it to lipsticks. Therefore, glycerin has been added in the form of W/O elusion, using low HLB emulsifier. Since EPDME is highly soluble in the oily components of lipsticks, it can be added directly to lipsticks (oily bases) without requiring any particular arrangement. EPDME thus added to lipsticks showed excellent effects to the lip.

5. CONCLUSION

EPDME showed to be less sticky and to have the following effects: (1) high moisture-retaining effect, (2) prevention of dry skin and (3) improvement of dry skin by daily application. It was also found that the application of EPDME in combination with glycerin resulted in synergistic effect to the dry skin.

When EPDME was added to lipsticks (oily bases), high moisture-retaining effects were noted. Daily application of this lipstick improved the lip. These results indicate that the protective effects of EPDME can be exerted even when it is added to oily bases such as lipsticks.

As shown in this study, EPDME is ease to handle and shows skin-care effects either in aqueous base or oily base. This is therefore a very useful raw material of cosmetics. Controlling its polarity and physical properties, this material will be applicable to a wider range of cosmetics formulae.

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