Characteristic of hydrophobically-modified hydroxypropyl methylcellulose, and application of hair cosmetics.

Abstract : Hydrophobically-modified hydroxypropyl methylcellulose (HM-HPMC) is a thickener which has hydrophobic long chain alkyl group in molecular side chain. Because of the interaction of hydrophobic group in water, HM-HPMC has a good viscosity increase and thixotropic characteristics in comparing with hydroxypropylcellulose (HPC) and hydroxyethylcellulose (HEC).
By formulating HM-HPMC in hair care product, it was possible to develop the product which is excellent in the growth to hair, pliability, slide property, and freshness.
This paper describes the result of basic physical properties of HM-HPMC for hair care product and one of applying HM-HPMC to hair treatment, and manufacturing notes.

Keyword Hydrophobically-modified hydroxypropyl methylcellulose ; HM-HPMC ; thickener ; hair care ; hair treatment

1. Introduction

Cellulose derivatives have been applied to various cosmetic areas including viscosity adjustment, thickening, gelatinization, dispersion stabilization, water retention, emulsion stabilization, adhesion and film formation depending on their characteristics. Particularly, hydroxypropylcellulose (HPC) and hydroxyethylcellulose (HEC) have been preferably used in the areas, such as viscosity adjustment, thickening and gelatinization, in the system in which carbomer, a typical thickener, cannot be used (compounding with cationic components, etc.). However, thickening efficiency is limited with these cellulose derivatives because of their molecular weights; therefore, it is necessary to add them in a considerable quantity to obtain desired viscosity. Moreover, in comparison with carbomer, solutions prepared from the cellulosed derivatives show poor thixotropicity, giving unsatisfactory results with respect to the sense of use as cosmetic preparations.

On the other hand, it has been tried to improve thickening efficiency and sense of use by introduction of hydrophobic functionalities such as C12 to C18 side chains into existing cellulose derivatives. For example, derivatives have been prepared by introduction of C12 to C16 side chains into HEC (hereinafter, referred to as HM-HEC), and an application of such derivatives to shampoo has been reported.[1)] HM-HEC has been positioned as a surfactant rather than a thickener because of the points that low-molecular weight HEC is used as a raw material for structural modification, and that its molecular structure has been designed so that the degree of substitution of the

hydrophobic group becomes relatively high.

Moreover, a study of the use as gelatinizing agents for pharmaceutical products by introduction of hydrophobic groups into macromolecular cellulose derivatives has also been reported.[2)] In the reported study, hydrophobic HPMC (hereinafter, referred to as HM-HPMC) was synthesized for evaluation by introduction of a C18 hydrophobic group using high-molecular weight HPMC (hydroxypropylmethylcellulose) as a cellulose derivative. The limiting viscosity and apparent viscosity of the aqueous solutions of HM-HPMC and its raw material HPMC were measured for comparison, showing no difference in the limiting viscosity that reflects the size of pure macromolecules, while the apparent viscosity that affects the dispersion of macromolecules and interactions between them in the measurement system was found to be markedly higher in the HM-HPMC solution than that in the HPMC solution. Based on this finding, it was discussed that the thickening efficiency of HM-HPMC might be related to the formation of an inter-molecular network by molecular association among the hydrophobic groups in water. In addition, it has also been reported that thixotropic fluidity similar to carbomer is exhibited by formation of the network like this.

HM-HPMC is marketed under the INCI name of "Hydroxypropylmethylcellulose Stearoxy Ether", and it has become to be used in various cosmetic areas commencing with skin care and hair care.

2. Viscosity Characteristics of HM-HPMC

The relationship between the quantity of addition of HM-HPMC aqueous solution and its raw material, HPMC, and viscosity is shown in Figure 1. Despite no great difference in the length of the main macromolecular chain between HM-HPMC and HPMC, HM-HPMC shows thickening efficiency superior to HPMC. Similarly, the relationship between the shear rate and viscosity of the 2 types of aqueous solutions was examined (Figure 2). It was revealed that HM-HPMC showed a greater decrease in apparent viscosity with increase in shear rate, forming a more thixotropic aqueous solution compared to HPMC. It is considered from the above findings that preparation of a formulation with better sense of use may become possible by use of HM-HPMC as a thickener by addition to cosmetic preparations in a smaller quantity.

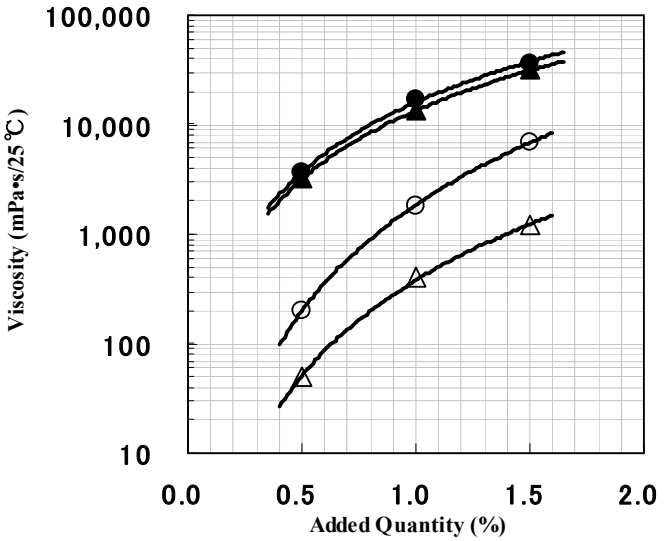

Figure 1: Relationship between the Quantity of Addition of Cellulose Derivatives and Viscosity

B-Type viscometer, 6 rpm (25℃)

○ HPMC (viscosity grade: 100,000)

△ HPMC (viscosity grade: 10,000)

● HM-MPMC (viscosity grade: 100,000)

▲ HM-MPMC (viscosity grade: 10,000)

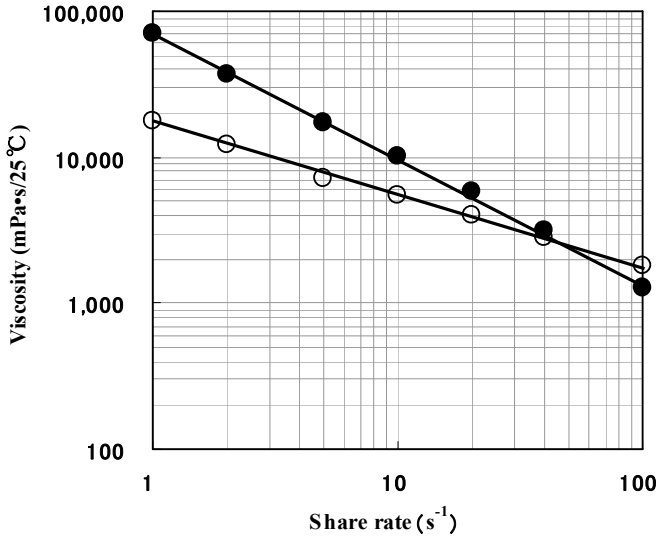

Figure 2: Relationship between Shear Rate of Cellulose Derivatives and Viscosity

E-Type viscometer (25℃); quantity of addition of cellulose derivatives: 1.0%

○ HPMC (viscosity grade: 100,000)

● HM-MPMC (viscosity grade: 100,000)

3. Anticipated Functions Obtained by Introduction of HM-HPMC into Hair Care Products

Negative senses of use such as tangling of the hair and friction or bad passing of the fingers through the hair at washing due to the sense of bundling, or sense of stiffness/roughness at drying are associated in many macromolecular thickeners that are compounded in hair care products, when they are excessively adsorbed. The majority of consumers tend to desire the natural texture (sense of smoothness or cohesiveness) that the hair originally has. HM-HPMC exhibits very high thickening efficiency at a low concentration, with which viscosity is easily adjustable, while the texture of the natural hair is being retained; therefore, its compounding in hair care products is considered useful.

Moreover, not only the functions as a thickener, it is also expected for HM-HPMC that it may be effective in protecting hair and imparting good sense of use to hair care products. The lipid layer called F-layer is present in the outermost surface of the cuticle covering the hair surface, making the hair surface hydrophobic. At the same time, 18-methyleicosanoic acid contained in the lipid layer has the function to impart a smooth texture to the hair surface. The hydrophobic F-layer that has originally been present in the hair surface is lost partly or fully by repeated chemical treatments such as coloring and permanent waving, through which hair surface becomes hydrophilic. Like this, friction and hair tip tangling may occur at hair washing and drying, respectively, by hydrophilization of hair surface. The hydrophilic part in the HM-HPMC molecule has an affinity to the hydrophilic damaged area of the F-layer, while frictional resistance is reduced by hydrophobization of the hair by the presence of a hydrophobic long-chain alkyl group, through which the effects, such as good passing of the fingers through the hair and the smoothness of hair surface, etc., can be expected. Furthermore, since HM-HPMC possesses an amphiphilic property, it exists in the vicinity of the interface between lipid and water in emulsified bulk, through which the interfacial film is hardened. Thus, it is expected that stability of lipid particles may be heightened by HM-HPMC, and that it may function as an auxiliary emulsifying agent.

4. Characteristics in the Use for Hair Treatment

The characteristics of HM-HPMC in the use for hair treatment were examined.

4-1. Properties of Aqueous Solution of HM-HPMC and Sense of Use

The appearance of 1% aqueous solution of HM-HPMC is a light yellow and clear gel. The gel is not hard, while it having elasticity, being well spread on the palm.

4-2. Texture

Evaluation Method: An aqueous solution of 1% HM-HPMC and aqueous solutions of other thickeners were prepared, and 40 g each of the solutions was applied to the whole head in 10 study subjects of 20's to 50's in age having middle-damaged hair, and their hair was washed after standing for 5 minutes, then the hair was set using a hair dryer. Sensory evaluation was made by 5-ranked rating (Table 1) at wetting and drying.

Table 1: Criteria for Sensory Evaluation

	Spread on the hair	Hair elasticity	Hair slide property	Hair freshness
5 Points	Good	Soft	Good	Good
4 Points	Slightly good	Slightly soft	Slightly good	Slightly good
3 Points	Normal	Normal	Normal	Normal
2 Points	Slightly bad	Slightly hard	Slightly bad	Slightly bad
1 Point	Bad	Hard	Bad	Bad

Evaluation Results: HM-HPMC was well spread at both wetting and drying, giving an excellent sense of use with its distinctive gel property. Furthermore, it was found that HM-HPMC was effective in imparting high elasticity and natural slide property to the hair through hair surface hydrophobization by its hydrophobic functional group (Tables 2 and 3).

Table 2: Results of Sense of Use and Hair Sensory Evaluation at Wetting

	Spread	Elasticity	Slide property
1% HM-HPMC	4.3	4.6	4.3
1% HEC	2.4	2.4	2.9
1% Highly polymerized PEG	4.0	1.4	1.4
1% Guar gum	2.4	2.6	3.0
1% Carrageenan	3.0	2.6	3.0
1% Konjac mannan	3.1	3.0	3.0

Table 3: Results of Hair Sensory Evaluation at Drying

	Elasticity	Slide property	Freshness
1% HM-HPMC	4.6	4.6	3.6
1% HEC	1.4	2.9	1.4
1% Highly polymerized PEG	1.4	1.4	1.4
1% Guar gum	3.0	3.0	2.7
1% Carrageenan	3.1	3.0	2.7
1% Konjac mannan	3.0	3.0	2.6

4-3. Observation at the Time of Application to Damaged Hair

The hair of a Chinese was treated as described below, and it was examined by a scanning electron microscope (Model TSM-6701F, JEOL Ltd.).

Method for Treatment of Damaged Hair: The hair was bleached in a mixture of 10% hydrogen peroxide and 10% ammonia water (1:1) for 50 minutes, then it was washed with water and dried using a hair dryer (Figure 3).

Treatment with HM-HPMC: An appropriate amount of 1% aqueous solution of HM-HPMC was applied homogeneously to the damaged hair described above, and then it was washed with water and dried using a hair dryer (Figure 4).

In accordance with the results obtained by the sensory evaluation, an improvement in the state of hair surface could be found by treatment with HM-HPMC.

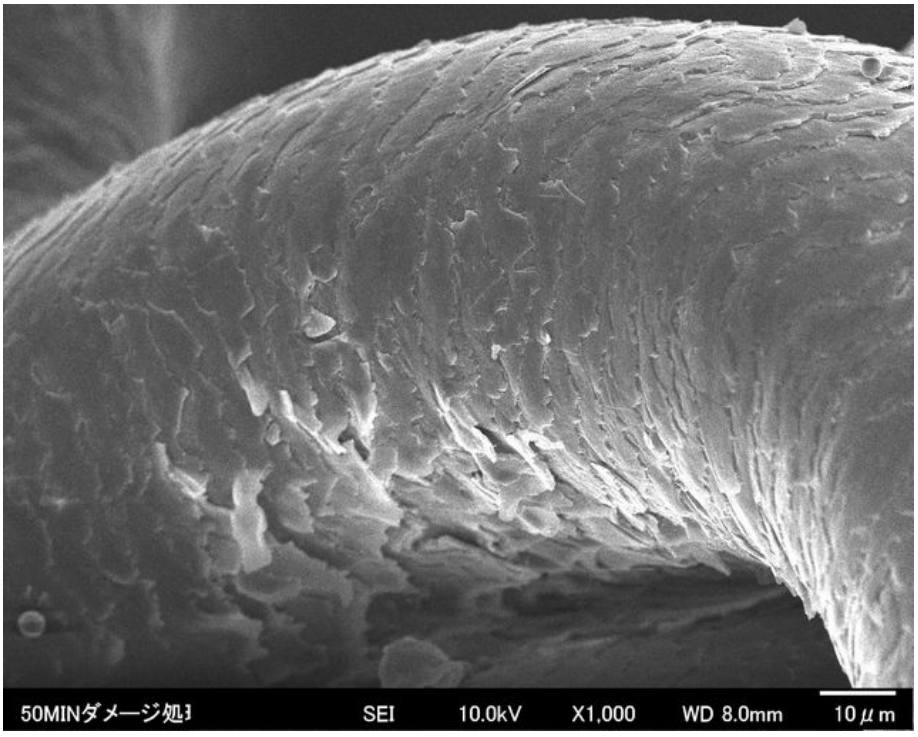

Figure 3: Electron Microscopic Picture of Damaged Hair

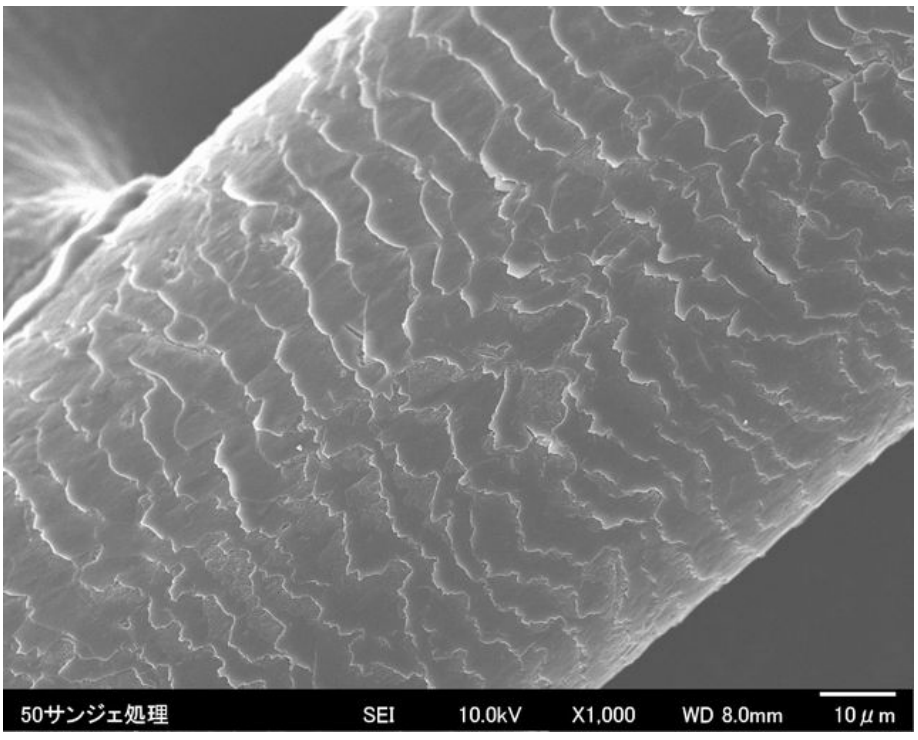

Figure 4: Electron Microscopic Picture of Damaged Hair Treated with HM-HPMC

4-4. Stability

Multiple thickeners are occasionally used for the purpose of improvement in product stability, etc.; thereby, when HM-HPMC is used in combination with other thickeners, it is necessary to design the formulation with caution because the combination use may affect water solubility of HM-HPMC. Particularly, when it is used in combination with guar gum, HEC, etc., it is desirable to carry out product stability test with caution, because some cases of separation were found with time. Moreover, when it is used in combination with polyhydric alcohol components, such as higher alcohols and glycerin, etc., or certain antiseptics, there are occasionally cases of separation and decrease in viscosity; therefore, it is necessary to decide compounding conditions with adequate precaution.

4-5. Irritancy to the Scalp

A patch test was performed to confirm irritancy of HM-HPMC to the scalp.

Test Method: A 24-hour occlusive patch test of the upper inner arm was performed using Finn Chamber®.

Test Samples:

i) 1.2% Aqueous solution of HM-HPMC

ii) Purified water (negative control)

iii) 0.5% Sodium lauryl sulfate (positive control)

Judgment Method: Sin reaction was judged by visual inspection 2 hours after application.

Calculation Method: Primary irritation index (P.I.I.) was calculated by dividing the total sum of the larger value of skin reaction either 2 or 24 hours after application by the number of study subjects using the following equation:

$$\text{Skin irritation index} = \frac{\sum (\text{Larger value of the skin reaction either 2 or 24 hours after application})}{\text{Number of study subjects}}$$

Evaluation Criteria: Skin irritancy was rated by scoring the safety categories (Table 4).

Table 4: Skin Irritation Index and Safety Category

Primary Irritation Index (P.I.I.)	Safety Category
0 ～ 0.5	Not irritating
0.5 ～ 2.0	Mildly irritating
2.1 ～ 5.0	Irritating to a comparable degree
5.1 ～ 6.0	Strongly irritating
6.1 ～ 8.0	Corrosive

Evaluation Results: The safety category of HM-HPMC was rated as a non-irritating substance, being judged not to be problematic in the irritancy to the scalp (Table 5).

Table 5: Irritancy Evaluation Results

Judgment Time	1.2% HM-HPMC	Purified Water	0.5% Sodium Lauryl Sulfate
After 2 hour	0.0	0.0	0.6
After 12 hours	0.1	0.0	0.8

5. Application of HM-HPMC to Hair Treatment

Operational performance, sense of use, issues, etc., at application of HM-HPMC to hair treatment, including comparisons with other macromolecular thickeners, are reported here.

Examinations were made for the 2-agent treatment systems in which an insoluble product is formed by complexation of an anionic polymer and a cationic surfactant (Table 6).

Table 6: Formulation For Evaluation of Treatment Agents 1 and 2

<Treatment Agent 1>

	1-A	1-B	1-C
HM-HPMC	0.50	—	—
HPC	—	1.10	—
HEC	—	—	1.00
Polyglutamic acid	0.55	0.55	0.55
Paraben	0.22	0.22	0.22
Purified water	Residue	Residue	Residue
Viscosity (mPa•s)	16,700	17,200	16,300

Viscosity: B-Type viscometer, 12 rpm, 25°C

<Treatment Agent 2>

Stearyl trimethyl ammonium chloride	2.00
Cetyl alcohol	5.00
Isopropyl myristate	4.50
Purified water	Residue

Polyglutamic acid was compounded as an anionic polymer in the treatment agent 1. In addition, a macromolecular polymer was used as a thickener to adjust viscosity so that the agent can easily be applied to the hair. A cream formulation consisting mainly of a cationic surfactant was prepared as the treatment agent 2 aimed at formation of an ionic complex by mixing with the agent 1.

Using these trial products, effects of difference in the type of thickener on the property related to sense of use were assessed by the sensory test (Table 7).

Table 7: Sensory Evaluation Results of Hair Treatment

<At wetting>

	Spread(Operational performance)	Elasticity	Slide property
1-A	1.3	3.5	3.8
1-B	3.0	2.7	2.5
1-C	3.6	2.5	2.1

< At drying >

	Elasticity	Slide property	Freshness
1-A	3.5	4.2	3.8
1-B	2.3	2.7	2.1
1-C	2.0	2.5	1.9

It was possible to obtain comparable viscosity by addition of HM-HPMC in a smaller quantity compared to other 2 types of thickeners. Moreover, it was revealed with respect to the sense of use that HM-HPMC was superior to other 2 types of thickeners in the points that it showed better slide property and lower tendency in hardening of the hair at wetting, and that a better texture in elasticity/moisture retention could be imparted to the hair with its better slide property at drying. However, although issues remained unsolved with respect to the operational performance at spreading on the hair and covering power at application, because of the excessive hardness of the gel from the characteristic as hair treatment product (brushing) when HM-HPMC is used as it is, the issues could be

improved by combination use of an emulsion, through which gel hardness could be reduced. In addition, it became also possible to impart emollient property by combination use of an emulsion. Examples of the combination use were shown in Table 8, and the sensory evaluation results were shown in Table 9.

Table 8: Examples of Formulation by Combination with an Emulsifying System

HM-HPMC	0.40
Polyglutamic acid	0.05
Cetyl alcohol	2.00
Behenyl alcohol	1.00
Octyl dodecanol	2.00
Cetyl ethylhexanoate	5.00
Decaglyceryl *tris*-stearate	0.80
Polyoxyethylene cetyl alcohol (30 E.O.)	1.20
Purified water	Residue

Table 9: Sensory Evaluation Results of Hair Treatment by Compounding of an Emulsifying System

<At wetting>

	Spread(Operational performance)	Elasticity	Slide property
1-A'	3.7	3.5	4.2

< At drying >

	Elasticity	Slide property	Freshness
1-A'	3.5	4.2	3.8

Since it was difficult to impart emollient property with the other 2 types of thickeners from the stability aspect, the finding may suggest an important characteristic of HM-HPMC.

Assuming actual production, precautions for compounding of HM-HPMC were described in the following.

Although HEC and HPC are marketed, which are claimed to be soluble at ordinary temperatures, they tend to form an insoluble mass when they are added to water at ordinary temperatures, being difficult to dissolve. For complete dissolution, it is necessary to add and disperse in water that has previously been heated to a temperature (75 to 80°C) at which it is insoluble, and then cool it to 25°C; therefore, the relevant operational time becomes additionally necessary in the manufacturing process.

Occasionally, complete dissolution may become difficult in the presence of other highly water-soluble components at addition of HM-HPMC; therefore, it is necessary to take it in mind that the operation may become tedious when heating and cooling processes are necessary for emulsification like as the present example, in addition to heating and cooling in the process for dissolution of thickeners. The differences in finish by difference in manufacturing process were shown in Table 10.

Table 10: Differences in Finish by Manufacturing Process of the Formulations Shown in Table 8

Phase A: HM-HPMC, purified water (50% of the compounded quantity) Phase B: Cetyl alcohol, behenyl alcohol, octyl dodecanol, cetyl ethylhexanoate, decaglyceryl *tris*-stearate, polyoxyethylene cetyl ether (30 E.O.) Phase C: Polyglutamic acid
<Manufacturing Method 1> 1) Preparation of A-Phase: Add HM-HPMC to purified water that has previously been heated to 80°C with stirring, and disperse it in water. Then, cool the mixture to 25°C to dissolve HM-HPMC. 2) Separately, mix the B-phase that has been heated to 80°C in another tank by a homogenizing mixer, and stop the homogenizing mixer after emulsification. Then, gradually add the remaining purified water that has been heated to 80°C and used for preparation of the A-phase with stirring by a paddle mixer. 3) Stop the homogenizing mixer, and add the prepared A-phase to the mixture. Mix adequately, and cool the mixture to 25°C. 4) After cooling, add the C-phase to obtain the formulation of cream for evaluation.
<Manufacturing Method 2> 1) Modify the method for preparation of the A-phase described in the above manufacturing method 1 as follows: omit the process of cooling to 25°C after dispersion of HM-HPMC at 80°C (Add it in the process 3) at the temperature of 80°C). Processes of 2), 3), 4) are the same as in the manufacturing method 1.
<Results> The formulation prepared according to the "manufacturing method 1" became a slightly hard cream. On the other hand, the formulation prepared according to the "manufacturing method 2" formed a precipitate of insoluble HM-HPMC.

As described above, although there are some points to consider, it is possible to design products having unique characteristics in both physical property and sense of use at the same time by application of HM-HPMC to hair treatment.

6. Conclusions

Carbomer has been the main stream of cosmetic thickeners to date. Moreover, although various cellulose derivatives or natural macromolecules have been used in the systems in which carbomer cannot be used, those having satisfactory properties not only in thickening efficiency but also in the sense of use have been available little.

It was revealed by the present study that HM-HPMC might be advantageous in the points not only that it exerted excellent thickening efficiency, but also that various functions were imparted to hair care products by its structural characteristic. It is considered that HM-HPMC may be a raw material with which further applications can be expected in the future.

HM-HPMC
INCI name : Hydroxypropylmethylcellulose Stearoxy Ether
Trade name : SANGELOSE
Manufacturing company : DAIDO CHEMICAL CORPORATION (Japan)
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