Journal of the University of Chemical Technology and Metallurgy, 42, 2, 2007, 187-194

THE CHOICE OF THE THICKENER - A WAY TO IMPROVE THE COSMETICS SENSORY PROPERTIES

M. Karsheva, S. Georgieva, S. Handjieva

University of Chemical Technology and Metallurgy
8 Kl. Ohridski, 1756 Sofia, Bulgaria
E-mail: mik@uctm.edu

Received 05 September 2006
Accepted 12 February 2007

ABSTRACT

The proposed study investigated rheological behaviour of different cosmetic products in order to compare some types of cosmetic thickeners used for the preparation of cleansing products as shampoos and douche gels as well as for cosmetic gels with different properties. Experimental information derived from the samples studied exhibit non-Newtonian behaviour, which involves description by the power-law rheological model. Its parameters were found statistically from the experimental data. It was proved that similar flow properties could be obtained using of different thickening agents: electrolytes, cellulosic or PVA in water solutions. So, the choice of the proper thickener should be made in dependence of its other useful properties and its price. In the same time the effect of different cosmetics ingredients during formulation was studied.

Keywords: rheology of cosmetic products, thickener choice, influence of different ingredients on flow properties.

INTRODUCTION

The thickening agents are an important part of cosmetic formulating, offering an opportunity not only to regulate the product viscosity, but also to improve the rheological properties of stability, feel and flow. The requirements for different cosmetic products' flow properties are different, too. In this study the viscosity regulation of cleansing products as shampoos and douche gels as well as of cosmetic protection creams will be presented.

Background

There are a number of ways to increase the viscosity of certain product, such as adding solids, increasing the internal phase ratio, homogenization or adding thickeners [1].

More than 500 thickeners are listed in INCI dictionary. The choice of the proper one often is more art than knowledge. Unfortunately the "universal thickener" does not exist yet. However, certain ingredients are often used, so the basic ingredient groups will be focused.

Aqueous thickeners: cellulose and its derivatives; clays; gums, PEGs and their modifications; synthetic polymers.

Non-aqueous thickeners: organics; organoclays; polyethylenes; silicas.

In [1] a comparison of the most often used thickener properties is presented (Table 1).

Shampoos formulation and viscosity regulation

Shampoos are based on complex systems of surfactants and their basic function is to cleanse the hair. Because of everyday usage of these products, it is not surprising that the shampoo market for example, comprises approximately 12 % of the personal-care industry [2]. These products are complex systems, consisting of about 80 % of water, 10 % of surfactants, less than 5 % of viscosity modifiers, about 2 % of preservatives, fragrance and colorants and about 3 % of performance additives [3]. The **primary surfactant** is the key foaming/cleansing agent of the shampoo. One of the most popular primary surfactant is sodium lauryl sulphate (SLS). Recently it is partly replaced by ammonium lauryl sulphate (ALS) [4]. The **secondary surfactant** is very often used to reduce the drying effect of the primary surfactant and to modify the aesthetic properties of the shampoo. The most popular secondary surfactant is the ether sulphate analogue of the primary surfactant. The second most popular secondary surfactant is the betaine. Betaines (usually cocamidopropyl) have a permanently quaternized nitrogen. Because of that they could be a good hair conditioning agent and also complexed with the sulphate to build the viscosity and to improve the clarity [4].**Viscosity builder.** Few things are more important to the consumers than using a thick (rich) shampoo, directly correlating that with the value and the concentration. The shampoos are expected not only to be easy to use, but also to meet sensory criteria that will appeal to the customer. The thickness and the flow characteristics of shampoos are described by the term "viscosity". Viscosity affects both the cleansing efficiency and the consumer perception of a product. The rheology affects also the foaming properties, production filling, packaging, storage and stability of the product [5]. There are many rheological additives possible for usage in cosmetic chemistry. Their choice depends both on the desired rheological properties of the final product and the compatibility of the thickener with the other components in the composition. Historically alcanoamides first have been used to increase the viscosity. But it was found that they do not actually build-up viscosity but only change the position of the "salt curve", or in other words less salt is required to increase the viscosity. Other more effective viscosity builders include betaines. They make complex with anionics to form an enlarged surfactant micelle that build the viscosity. Additionally they contribute electrolyte (sodium chloride) that also builds the viscosity. Electrolytes are almost always used to build the viscosity of shampoos. They are inexpensive and effective [4].

Cosmetic gels formulation and viscosity regulation

Recently the importance of sun protecting compositions, as gels, emulsions, creams etc increases more and more due to existing problems with the sun activity. During their formulation the same problems with viscosity regulation as in the case of cleansing materials appear. Moreover in these compositions different sun protection ingredients must be included as well as softening agents as different oily plant extracts. So, it is important to follow the dependence of the composition rheological parameters on different ingredients.

Cellulose derivatives

Cellulose is an effective thickener in water-based systems, as already mentioned. Cellulose-derived thickeners are among the most widely used thickeners in all types of cosmetic products as well as in the pharmaceutics due to their physical and sensory characteristics. They are commonly employed as bases in topically applied antiflammatory drugs, in the control release of drugs in the production of shampoos, solar filters, etc. [6-9]. Cellulose thickeners vary based on the method of addition, cost and viscosity characteristics provided. These materials are water-soluble polymers. To be effective, cellulosic thickeners are restricted to aqueous systems with high water content (>90 %). Only a small amount (about 10 %) rests for the surfactants and solids. These types of materials are compatible with a wide variety of cosmetic materials including anionic and cationic surfactants, electrolytes and non-ionic materials. The most common of these cellulosics are methylcellulose, hydroxypropylmethylcellulose and hydroxyethylcellulose. Cellulosic derivatives build viscosity because of their high molecular mass. Usually they exhibit substantional shear-thinning or pseudoplastic behaviour [8]. The powdered materials are hydrophilic in nature and readily swell in the presence of water. They are typically used at 1 % of level.

In our case methylcellulose (MC) was chosen as thickener in quantity of 3 % mass. It is well known that solutions with higher concentrations (> 4-5 %) of cellulosics in water exhibit clear elastic properties and are difficult to handle (cases of mixing and transport). Besides MC is easy to be combined not only with water-soluble, but also with oily components.

Surfactants

The role of the surfactants is essential to provide long-term stability to emulsions, since they prevent droplet coalescence by adsorbing at the o/w interface and increasing the repulsive interactions among droplets according to two main mechanisms: steric and electrostatic [10]. The former is peculiar to non-ionic surfactants and presents some technological advantages on the latter as intensity to the ionic strength and efficiency in the ionic and non-ionic media. Another way of enhancing the stability of emulsions and other disperse systems, limiting the oil creaming, and thus the formation of separated layer at the top of the system is based on addition of the polymers as thickening agents. In our case one of the wide spread surfactants, Na-laurylethersulfate was used. It is known as "GENAPOL LRO" (Hochst - Germany), "Tenzajeks SPDL" - (Tenesia - Belgium), "EMPICOL ES-B" - (Henkel-Germany).

In recent years, cosmetic oils of plant origin as well as the oily extracts of plants have been reintroduced into the market, following consumers' demand for natural cosmetics. The plant extracts (thyme and calendula) with olive oil and the glycerol were used as components of solar protection gels' compositions.

UV absorbers [15]. In order to prevent the photo destruction of the components in the compositions as well as to neutralize the negative effect of UV radiation on the skin and the hair the following organic UV-absorbers were used in the compositions:

a) Escalol 557 (octylmetoxycinnamat) - commercial product, with an intensive absorption at wave length λ of 318 nm.

b) For the purposes of this work in the Department of Organic synthesis in UCTM-Sofia was synthesized 4-ethoxy-2-hydroxybensophenon with absorption maximum 338 nm.

All the products provide an effective protection in wide range of UV spectrum.

UV screen. Fine powder of TiO_2 was used as UV screen. The UV protection properties of TiO_2 suspensions are well known. Recently studies on the relationship between the rheological properties of such suspensions and their skin protection ability appeared in the literature [11].

The aim of this work was to compare different methods of cosmetic products' thickening.

EXPERIMENTAL

Materials and Methods

The rheological behaviour of shampoos, douche-gels and sun protection gels during their formulation was studied. For rheological measurements a co-axial cylinder viscometer Rheotest RV2 (Germany) with S1 cylinder was used. Unique experiments with cylinder S2 showed no slip effect of the compositions studied.

RESULTS AND DISCUSSION

Shampoos and douche-gels

In Table 2a the compositions of two industrially made shampoos ("Green apple" and "Eggs") are

Table 1. Comparison of thickener properties [1].

Thickener	Compatibility	Rheology	Yield stress	Electrolyte stability
Aq. thickeners				
cellulose gum	water	thixotropic	yes	yes
guar gum	water	pseudoplastic	no	yes
xantan gum	water	pseudoplastic	yes	yes
hydroxyethylcellulose	water	pseudoplastic	no	yes
methylcellulose	water	pseudoplastic	yes	yes
polyethylene glycols	water	Newtonian	no	yes
clays	water	thixotropic	yes	yes
Non-Aq. thickeners				
polyethylenes	Oil	pseudoplastic	yes	
trihydroxystearin (organic)	oil	thixotropic	yes	
organoclays	oil	thixotropic	yes	
fumed silica	oil	thixotropic	yes	

Table 2a. Compositions of “Green apple”, and “Eggs” shampoos.

No	Component, %, mass	a) Shampoo’s composition							
		1	1’	2	2’	3	3’	4	4’
1	Texapon	7.5	9.0	7.5	9	7.5	9	7.5	9
2	Empigen BB			1	1.5	1	1.5	1	1.5
3	Empilan250			1.4	1.0	1.4	1.0	1.4	1.0
4	Fragrance			0.3	0.2	0.3	0.2	0.3	0.2
5	Euksil			0.06	0.06	0.06	0.06	0.06	0.06
6	Alantoin					0.1		0.1	
6	Empipurl						1.5		1.5
7	Eggs flour						0.1		0.1
7	NaCl							3.5	3.3
8	Water	92.5	91.0	89.74	89.8	89.64	86.64	86.14	83.34

Table 2b. Rheological parameters of the compositions studied.

	$K_{green\ apple,}$ $Pa.s^n$	$n_{green\ apple}$	$K_{Eggs}Pa.s^n$	n_{Eggs}
1,1’	0.0852	0.6219	0.0522	0.5288
2,2’	0.0411	0.5607	0.0605	0.5075
3,3’	0.0235	0.6272	0.0556	0.5392
4,4’	3.3357	0.7568	21.569	0.3617

presented. The products were formulated using the same constituents as in industrial practice. On each step of formulation the rheology of compositions was followed. More detailes are given elsewhere [12]. Both products were chosen because of their compositions which differ quite slightly. They are based on two surfactants and an electrolyte (NaCl) as a viscosity builder. Both products exhibited non-Newtonian behavior which could be described by the power-law rheological model.

$$\tau = K.\dot{\gamma}^n \qquad (1)$$

here t is the shear stress, Pa, $\dot{\gamma}$ is the shear rate, s^{-1}, K is the consistency index, $Pa.s^n$, characterising the product consistency, n is dimensionless flow index. When n < 1 the fluids are shear-thinning (their apparent viscosity is decreasing with shear rate increase) and in the contrary, when n > 1 the products are shear thickening (their apparent viscosity increases with shear rate increase). More n differs from unity, more non-Newtonian is the fluid. The values of power-law model parameters K and n were found statistically by least squares method. They are summarized in Table 1b.

From Tables 2a and 2b it could be seen that even with quite serious difference in surfactants quantities, the basic thickening resulting in steep increase of the consistency index and decrease in flow index emerge after the electrolyte addition. For both products its quantity was verified by obtaining the salt curve. From the Table 2b it is evident that the NaCl addition in an optimal quantity [12] leads to the increase in consistency index 142 times for the “Green apple “shampoo and almost 385 times for the “Eggs” shampoo. In the same time the flow index for the first product changed slightly, for the second one decreased 1.5 times.

In Table 3a the compositions of shampoos and douche-gels, based on hydroxyethylcellulose (HEC) and polyvinilalcohol (PVA) water solutions are presented.

In Table 3b the values of the rheological parameters of the same compositions are summarized.

Table 3a. Cleansing cosmetics compositions.

No	Component, % mass.	Shampoo and douche-gel's composition							
		1	2	3'	4'	5'	6	7	8
1	Polyvinilalcohol	5	5	5	5	5			
2.	Hydroxyetylcellulose						1	2	2
3	"Empicol "			10	10		10	10	10
4	"Genapol LRO"		10						
5	"Nypagin"		0.2	0.2	0.2				
6	Isoamylcinnamate			0.2	0.2				
7	Rose concrete			0.2	0.2				
8	Tetraiodofluoroscein			1E-3	1E-3				
9	Boric acid	0.6	0.6	0.3	0.3				
10	KOH	7	7	6	6			7	7
11	Urea	1	1	1				1	1
12	Fragrance		0.1						0.1
13	Colorant		0.02						0.02
14	NaCl				2.5				
15	Water	87	77	77.37	75.6	95	89	89	89

Table 3b. Rheological parameters for shampoos and douche-gels for t = 25°C.

Shampoos			Douche-gels		
No	K, $Pa.s^n$	n	No	K, $Pa.s^n$	n
1.	1.9527	1.2275	3'.	19.2680	0.4568
2.	3.7658	0.9265	4'.	1.2683	0.6809
6.	1.3574	0.7129	5'.	0.0901	0.4686
7.	20.1470	0.5561			
8.	19.8250	0.5915			

From Tables 3a and 3b it could be seen that the pure 5 %, mass solution of PVA (composition 5') is pseudoplastic with very low consistency. The addition of KOH and boric acid, forming complexes with PVA, gives the solutions with dilatant properties (composition 1), changing again to pseudoplastic and much more consistent compositions with the surfactant addition (composition 3'). During the experiments two surfactants were used: EMPICOL and GENAPOL LRO. It is evident, that both led to the change in flow behaviour from dilatant to pseudoplastic (compositions 2, 3', 4'), EMPICOL enhancing the flow behaviour much more(compositions 2 and 3' – Table 3b). In this case the electrolyte addition leads to "dilution" of compositions (decreasing the consistency index and slight increase in flow index) due to incoherent quantity.

Compositions 6 to 8 are based on HEC as a gelating agent. From Table 3b it could be seen that the rheological behaviour of these compositions is pseudoplastic with rheological parameters basically influenced of HEC quantity. Its augmentation from 1 to 2 %, mass leads to increase in the consistency index almost 12 times and to comparatively slight decrease in flow index n values (1.2 times). The comparison between compositions 7 and 8 shows that the addition of fragrance and colorant to composition 7 quite slightly changes its rheological parameters.

We can now compare the flow behaviour of "Eggs" shampoo (Table 2 a, b – composition 4') with the HEC base shampoos (Tables 3a, 3b – compositions 7, 8). It is evident, that despite the different way of thickening (in the first case – electrolyte addition, in the

Table 4a. Cosmetic gels compositions studied.

Composition,mass%,No	1	2	3	4	5	6
hydroxyethylcellulose (HEC)	1	2	1	2	1	2
water	94	93	94	93	91	90
Na-laurylethersulphate	3	3	3	3	3	3
thyme/propilenglycol extract			2	2		
alkylpolyglucoside					3	3
calendula/olive oil extract	2	2			2	2

Table 4b. Rheological parameters of power- law model for the cosmetic compositions studied.

No	t, ^oC	K, $Pa.s^n$	n
1	24	0.3401	0.7325
2	24	2.8391	0.6205
3	24	0.5114	0.6721
4	24	4.9017	0.5366
5	24	0.6561	0.5449
6	24	1.9635	0.6415

second – thickening based on the use of water soluble cellulose derivatives) quite similar rheological behaviour of final products was obtained.

Cosmetic gels

Two different compositions with nourishing and sun protecting properties were prepared: one based on HEC in water solutions, another – on methylcellulose (MC) in water solutions. As for the cleansing compositions, the flow behaviour of preparations during their formulation was followed to find the influence of different ingredients and the operational conditions.

In Tables 4a, 4b the compositions and the rheological parameters of cosmetic gels are summarized. As for the case of shampoos (Tables 3a, 3b) they are based on HEC in water solutions in concentrations 1 and 2 %, mass. Evidently, in this case the anionic surfactant (Na-laurylethersulphate is in quite lower quantity necessary to stabilize the oil-in water emulsions. In some of the compositions (5 and 6) alkylpolyglucoside is included as a secondary nonionic surfactant. All compositions studied are power-law liquids, as already mentioned for this type of solutions. When comparing with compositions in Table 3a (6 – 8), it is clear, that for cosmetic gels the consistency is quite lower due to the smaller surfactant quantity (nearly 3 times) and to the extract addition. Comparing compositions 2 and 6 it could be seen the addition of nonionic surfactant (APG) "dilutes" the composition more, decreasing the consistency index nearly 1.5 times whilst the flow index n rests almost unaffected. In the same time the case with the smaller HEC concentrations is just the opposite: the APG addition leads to almost twice greater consistency and sensible decrease in flow index n (comparing compositions 1 and 5). A possible explanation of this fact could be the mechanism of thickening in the case of cellulosics. As it was already mentioned, cellulosic derivatives build viscosity because of their high molecular mass. They are hydrophilic in nature and readily swell in the presence of water. Except swelling and formation of net-like structures by the macromolecules, typical for them is also hydrogen binding and mycelia interaction as well as other intermolecular interactions when polyols or other compounds with high molecular mass are added to their solutions [13]. All these phenomena could affect the solution flow properties. An-

Table 5a. Sun protection gels compositions studied.

Composition,mass%,No	1	4	5	7	10	13	14
methylcellulose (MC)	3	3	3	3	3	3	3
water	97	93	90	90	95	90	90
Na-laurylethersulfate		4	4	4	4	4	4
thyme/glycerol extract							5
thyme /olive oil extract			5				
calendula/olive oil extract				5		5	
TiO_2 (UV screen)						0.3	0.3
ESCALOL 557 UV abs						1	1
4-etoxy-2-hydroxy-benzophenon-UVabsorber (UVA)					0.3		
fragrance composition						0.01	0.01

Table 5b. Rheological parameters of power- law model for the cosmetic compositions studied.

No	t, ^{o}C	K, $Pa.s^{n}$	n
1	24	91.371	0.2698
4	24	71.913	0.3054
5	24	14.834	0.4701
7	24	42.242	0.3791
10	24	45.864	0.3716
13	24	32.428	0.2594
14	24	18.934	0.4817

other possibility is the fact that combining the cellulosics with nonionic surfactants leads to certain viscosity decrease. So, according with the cellulosics and surfactant quantity used, the solutions could either increase or decrease their viscosities.

In Tables 5a, 5b the compositions and the rheological parameters of sun protection gels based on MC in water solutions are summarized. It can be seen that MC water solutions give much better thickening than those based on HEC solutions even without surfactant addition. The pure MC in water solutions exhibits the greatest consistency index values and the least flow index ones. Then the K values were found to decrease with other ingredients addition, in the same time the n values increased slightly, resting however quite smaller than those of HEC based solutions. An interesting fact was the observed influence of the type of plant extract added on the flow properties. The thyme-olive oil extracts represent lower K values (about 3 times) than those obtained after calendula-olive oil extracts addition (compositions 5 and 7 in Tables 5a, 5b).

CONCLUSIONS

The rheological behaviour of different cosmetic products during their formulation was studied. The aim of the investigation was to find the effect of different ingredients and especially the effect of different thickeners on the viscous properties of the final products. For their investigation some cleansing products (shampoos and douche gels) and cosmetic gels were chosen. The compositions were thickened by different ways: by the addition of 2 surfactants and NaCl as an electrolytic thickener; by the addition of PVA in water solutions with addition of different surfactants; by adding the water solutions of cellulosic derivatives (HEC and MC) and surfactant addition. It was found that all the compositions studied are non-Newtonian which involves their description by power-law rheological model. It was also found that despite the choice of different ways for cosmetic thickening, all the final products investigated exhibited apparent viscosities in the range $1 < \mu_{app} < 6\ Pa.s$ (for shear rate values of 13.5 s^{-1}) thus satisfying the market demands for such products [13,14]. Thus, the choice of the proper thickener for cosmetics should be made in respect to its other useful properties and its price.

REFERENCES

1. Dennis Laba, Allured's Cosmetics&Toiletries Magazine, **116,** 11, 2001, 35-44.
2. Drug Chain Review, .**22**, 2, 2000, 15-18, 21,22,24,26.
3. Hl. Leidreiter, U. Maczkiewitz, Utilizing Synergystic

Effects in Surfactant mixtures, Th. Goldschmidt AG, Essen, Germany, 1996.

4. Ken Klein, Cosmetics &Toiletries magazine, **119**, (5), 2004, 64-68.
5. Hl. Leidreiter, K.Jenny, U. Maczkiewitz, Th. Goldschmidt AG, D-45116 Essen, Germany 1995.
6. Dolz M., C.Rolden, J.V.Herraez, R.Belda, P.Sorbino, J.Dispersion Sci. and Technol., **13,** 1, 1992, 95-113.
7. M.J.Hernandez, J. Pellicer, J.Delegido and M.Dolz, J.Dispersion Sci. and Technol., **19**, 1, 1998, 31-42
8. A.M.Howe, A.E.Flowers, Allured's Cosmetics & Toiletries Magazine, **115**, 12, 2000, 63-69.
9. H.Plate, Hydroxyethyl Ethylcellulose. A new surface active hydrocolloid for use in personal care products. Cosmetics and toiletries manufacture world wide, 2000, 10th edition, 208.
10. S. Manca, R.Lapasin, P. Partal, C.Gallegos, Rheol.Acta, **40**, 2001, 128-134.
11. Akio Nasu, Yasufumi Otsubo, J. of Colloid and Interface Sci., **296,** 2, 2006, 558-564.
12. M.Karsheva, S.Georgieva, G.Birov, J Univ. Chem. Technol. Met. (Sofia), **40,** 4, 2005, 323-328.
13. D.Dimitrov, Teoria na kozmetichnite formi, Novateamcompact, Plovdiv, 2003, 94, (in Bulgarian)
14. S.Pascal, Demande de brevet d'invention, No 2755370, Composition nettoyante sous la forme d'un gel transparent rincable, 04.11.1996.
15. M.I.Santaro, Cosmetics&Toiletries Magazine, **115**, 2000.