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Rheological behavior of sun protection compositions during formulation

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Abstract−Rheological properties of cosmetic products are related to the products' sensory attributes and to performance. In literature there is a lack of information on the influence of physicochemical interactions during processing of complex systems. This study is focussed on the interactions between the ingredients of cosmetic compositions during formulation in respect to their flow behavior. The rheological behavior of model cosmetic compositions based on polyvinyl alcohol solutions and containing natural plant extracts in glycerol and olive oil, UV screens (TiO_2), synthetic UV absorber, emulsifier (Carbopol 2050), preservative (Bronopol) and fragrance was studied. The flow properties of compositions containing natural UV absorbers were compared to those of compositions with synthetic ones. All the compositions exhibited shear thinning rheological behavior that can be described by the power-law rheological model. It was proved that the emulsifier's addition thickens the compositions; the addition of Bronopol leads to slight degree of thixotropy avoided by pre-shearing the samples for one minute. The fragrance addition in EtOH solution lowers the composition's apparent viscosity; the addition of fine TiO_2 as UV-screen even in quite tiny quantity of 0.2% mass increases the consistency of basic 10% PVA samples, lowering in the same time the flow index. The compositions containing glycerol extracts are more stable than those with olive oil extracts and they preserve their properties longer.

Key words: Rheology, Sun Protection Cosmetics, Natural Plant Extracts

INTRODUCTION

In recent years emulsions have rapidly evolved in cosmetic preparations due to their high applicability and the technological advances on properties of raw materials. Despite their wide usage and economic significance, the development of cosmetic products, as well as the corresponding manufacturing processes, is normally conducted on a case-by-case basis. The rheological behavior of cosmetic products is one of the most important features not only from technical but also from the aesthetic point of view. These products are expected not only to be easy to use, but also to meet sensory criteria that will appeal to the customer. Rheological properties are often directly related to the product's sensory attributes and to its performance [1]. The manufacturing of toiletries is a complex procedure involving many possible process routes for a given formulation. The range of products is wide, from simple, low viscosity, single phase fluids to high viscosity non-Newtonian materials as creams, gels and toothpastes. In literature there is rich information on the physicochemical behavior of relatively simple systems, as well as on the suitability of different classes of equipment as mixers, pumps and reactors for their handling. But, with a few exceptions, there is a lack of information on the mutual influence of physicochemical interaction of the components during processing. Such interactions are likely to be especially important during the manufacturing of multiphase products consisting of many different ingredients. There are many possible to use in cosmetic chemistry rheological additives. Their choice depends both on the desired flow properties of the final product and the compatibility of the thickener with the other components in the composition. During the product formulation every additive plays its own role to affect the product's rheological behavior.

Recently, the interest in herbal pharmaceutical and cosmetic products has risen enormously. The traditional use of plants against skin diseases and especially for "cosmeceutical" purposes is a common practice in the domestic medicine of many cultures. Plant-derived home-made cosmetics, cosmeceuticals and remedies for skin diseases include approximately 135 preparations coming from roughly 70 botanical species. To prepare these formulations, people in southern regions as Italy, Spain, Southern France, etc. often use the maceration in olive oil [2]. The modern cosmetic industry recently turned to some of these traditional preparations. Modern phytocosmetics requires standardized defined extracts from herbal matrix. On the other hand, it is well established that the type of solvent as well as the type of the plant extract plays an important role in flow properties of the final products of phytocosmetics.

That is why the aim of this study was to investigate the dependence of flow behavior of sun protection gels during formulation and the influence of different operational conditions on their rheological parameters.

EXPERIMENTAL

1. Materials and Methods

As a gelling agent polyvinyl alcohol (PVA) solutions were used. **PVA** is a synthetic non-ionic polymeric compound with molecular

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mass between 50000 and 200000. Water-soluble polymers as PVA can be applied for different reasons. They can function as dispersive agents and as thickeners. Olive oil and glycerol are used for extraction. Olive oil has been used in cosmetics for centuries because of its humectant's properties quite beneficial to human skin [3]. Commercial 100% extra virgin olive oil (Romulo) was purchased from a local supermarket and used without any further treatment. Glycerol is a transparent liquid with sweet taste, liquid in low temperatures and infinitely soluble in water and ethanol. Being hygroscopic it could absorb nearly 50 % of water vapors from the air. The same property assures its effective humectant's action. On the other hand, its low volatility prevents water evaporation from the solutions. It has no toxic or allergic effects. These properties are the reason for the wide use of the glycerol in cosmetics. Calendula (*Calendula officinalis*) possesses a wide range of pharmacologic activity: antioxidant, regenerating, anti-inflammatory, antimicotic properties combined with hydrating, humectant's and sun protecting ones, which is the reason for its wide use in cosmetic in a form of different extracts. Its anti-inflammatory and wound-healing activity was documented in many experimental and clinical studies [4]. The *Hypericum Perforatum L.* (tutsan) extracts are also quite often used in cosmetics because of antibacterial properties. According to Italian tradition it is used in a preparation named "Oleum Hyperici" obtained by maceration of fresh flowers of *Hypericum Perforatum L.* in vegetable oils such as olive oil, sunflower oil or wheat germ oil; the final product is used for the treatment of wounds, especially burn wounds, bruises and swellings [5]. TiO_2 with mean particles size of 20-30 nm was used as UV screen. Octylmetoxycinnamat (OMC) (Escalol 557) is one of the widely used synthetic UV-absorbers with effective sun-protection action - commercial product, with an intensive absorption for wave length of 318 nm. Cinnamic acid (3-phenylpropenoic acid) and dihydroxybenzophenon being widely applied in cosmetics were also used as synthetic UV absorbers. The para-methoxy-cinnamates, such as OMC or isoamylmethoxycinnamate, undergo a photochemical reaction to form minute traces (in ppm) of an intensely yellow compound on the surface exposed to daylight [6]. Use of the plant extracts with sun-protecting action would lead to decrease of this color effect unpleasant for the consumers and difficult to handle in packaging. Easy to disperse (ETD) CARBOPOL 2050 was used as emulsifier [7]. The dispersions of these polymers in water are acid and highly fluid, with near-Newtonian rheological behavior at low polymer concentrations. It is well established [8] that the addition of neutralizing agent as sodium hydroxide, triethanolamide, etc., decreases the turbidity of the dispersion and considerably increases its consistency. The reason is an elongation of polymer chains due to electrostatic repulsion forces. The chains interlink to produce a water-retaining three-dimensional network, forming as a result a viscous transparent gel [9]. The physical and sensory characteristics of these gels make them very useful in pharmaceutics and cosmetics. They are commonly employed as bases in topically applied anti-

Table 1. Compositions studied

Composition, % mass	1.0	1.1	1.2	1.3	1.4	1.5	1.6	1.7	1.8	1.9	1.10	1.11	1.12
PVOH	10	10	10	10	5	5	5	10	10	10	5	5	5
H_3BO_3	0.2	0.2	0.2	0.2	0.2	0.2	0.2	0.2	0.2	0.2	0.2	0.2	0.2
0.1 n KOH	2	2	2	2	2	2	2	2	2	2	2	2	2
GCE		5	5	5	5	5	5						
TiO_2			0.2	0.2	0.2	0.2	0.2		0.2	0.2	0.2	0.2	0.2
GStJWE								5	5	5	5	5	5
Carbopol				0.3	0.2	0.2	0.2			0.3	0.2	0.2	0.2
Bronopol						0.2	0.2					0.2	0.2
Fragrance							0.02						0.02
Water	89.8	82.8	82.6	82.3	87.2	87.0	86.98	82.8	82.6	82.3	87.2	87.0	86.98
Total	100	100	100	100	100	100	100	100	100	100	100	100	100

Composition, % mass	1.13	1.14	1.15	1.16	1.17	1.18	1.19	1.20	1.21	1.22	1.23	1.24	1.25	1.26
PVOH	10	10	5	5	5	10	10	5	5	5	10	10	10	10
H_3BO_3	0.2	0.2	0.2	0.2	0.2	0.2	0.2	0.2	0.2	0.2	0.2	0.2	0.2	0.2
0.1 n KOH	2	2	2	2	2	2	2	2	2	2	2	2	2	2
OCE	5	5	5	5	5									
TiO_2		0.2	0.2	0.2	0.2		0.2	0.2	0.2	0.2			0.2	
OStJWE						5	5	5	5	5				
Carbopol			0.2	0.2	0.2			0.2	0.2	0.2				
Bronopol				0.2	0.2				0.2	0.2				
UV abs OMC														5
2,4 DHBPh												0.2		
Lavender oil											5	5	5	5
Fragrance					0.02					0.02				
Water	82.8	82.6	82.3	87.0	87.18	82.8	82.6	82.3	87.0	87.18	82.8	82.6	82.6	77.6
Total	100	100	100	100	100	100	100	100	100	100	100	100	100	100

inflammatory drugs, in the controlled release of drugs, in the production of solar filters, etc. [10,11]. As a preservative Bronopol BP 2000 (2-bromo-2-nitropropane-1,3-diol) was used. It also ensures a good medium or the natural plant extracts [12,13].

2. Extracts Preparation

The glycerol plant extracts were prepared as follows: the necessary quantity of the plant (5 g) finely chopped up was added into little quantity of 50% glycerol-in-water solution (10 cm^3). After some time the whole quantity of the glycerol (90 cm^3) was added. The suspension was left for 48 hours. Then it was filtered to obtain the final extract. The olive oil extracts were prepared by the same way. The only difference is the necessary time - about 5 days.

3. Gel Preparation

The basic gel was prepared by the following manner: at first a water solution of H_3BO_3 was placed into the flask with mixer and reverse cooler. Then into this solution the PVA was added and left for 1 hour to swell. After that the composition was mixed at 80 ºC for 1 hour. Then the temperature was lowered to 60 ºC and a 0.1 N KOH solution was added for pH regulation.

The emulsifying of the biologically active oily extracts in the basic PVA gels was done in a flask with intensive mixing (1,200 rpm) at 50 ºC during 1 hour.

In Table 1 all 35 compositions investigated are presented. Their rheological properties were studied using a co-axial cylinder viscometer Rheotest RV2 (Germany) with S1 cylinder for the temperature interval between 20 and 40 ºC. Single experiments with cylinder S2 showed no wall slip effect of the compositions studied. The whole range of shear rates from 1.5 s^{-1} up to 1,320 s^{-1} was investigated for all the compositions. In the results just the lower shear rates (up to 250 s^{-1}) are presented in the paper, for this is the range of practical interest (the spreading of the cosmetic creams is carried out at about 60 to 100 s^{-1} shear rates). Microscopic observations were made with OLYMPUS IMT, 40×10, equipped with Microcolor Camera Hitachi, Monitor Video Colour Hitachi CM-1821-A.

RESULTS AND DISCUSSION

In Fig. 1 typical flow curves for the compositions studied are presented. It is evident that all the compositions studied are shear thinning non-Newtonian liquids. To check the samples for thixotropy, for all the compositions were obtained the upward curve (corresponding to agitation time t=0) for increasing shear rates between 1.5 and 1,320 s^{-1} and the different downward flow curves (decreasing $\dot{\gamma}$ values) after agitation times up to 15 min. All determinations were repeated at least three times. Agitation was carried out with the same viscometer cylinder at maximal shear rate value of 1,320 s^{-1}. The shear stress (respectively, apparent viscosity was found to remain practically constant for all ccompositions without Bronopol (preservative) addition, i.e., these gels exhibited no noticeable thixotropic behavior. For the formulations containing Bronopol (see Table 1), slight degree of thixotropy was observed. After 50 seconds the equilibrium down-curve was reached. So, the measurements obtained after 1 min agitation time were considered in all cases. In the tables the data presented for thixotropic formulations are for the equilibrium curves.

The flow curves without intercept could be described by power-law rheological model of Ostwald-de Waele:

$$\tau = K\dot{\gamma}^n.$$

Here K ($Pa{\cdot}s^n$) is the consistency index, characterizing the consistency of the composition, and n (–) is the dimensionless flow index, characterizing the degree of the non-Newtonian behavior (more n differs from unity, the more non-Newtonian is the liquid). The rheological parameters of the power-law model were found by standard statistics. Their values are presented in Table 2. It is evident that even the water solutions of PVA are slightly shear thinning (n=0.9927). The addition of every other ingredient increases this behavior.

The comparison between the samples containing only 10% PVA-in-water solution (sample 1.0) and the solutions containing 5% mass of glycerol-calendula extract (sample 1.1) and 5% mass of olive oil-calendula extract (sample 1.13) shows that the flow index of PVA solutions decreases with 10%. In the same time the consistency of the compositions increases and this effect is much more pronounced in the case of olive oil extracts, forming emulsions with PVA solutions. The same comparison made between the glycerol and olive oil extracts of St. John's wort (tutsan) shows almost no influence of the solvent used (samples 1.0 compared to 1.7 and 1.18). The comparative samples made only with glycerol and olive oil in 10% PVA-in water solutions proved that the consistency of olive oil containing samples is always higher than that of glycerol containing ones (K for olive oil samples being about 8 times higher than K for the glycerol ones). So in this case the tutsan governs the flow behavior of the compositions, masking the thickening effect of the olive oil.

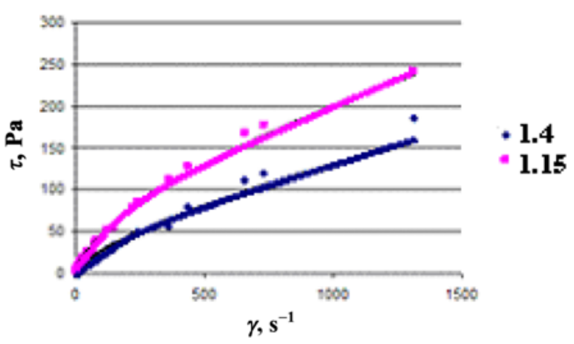


Fig. 1. Influence of the solvent on flow properties of calendula extracts containing formulations: 1.4-glycerol-calendula; 1.15-olive oil-calendula in 5 % PVA.

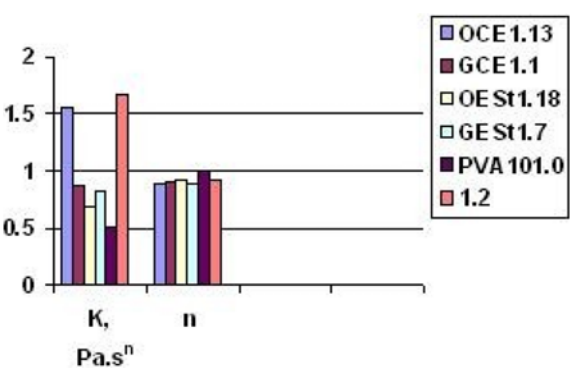


Fig. 2. Effect of the solvent and the plant on the rheological parameters.

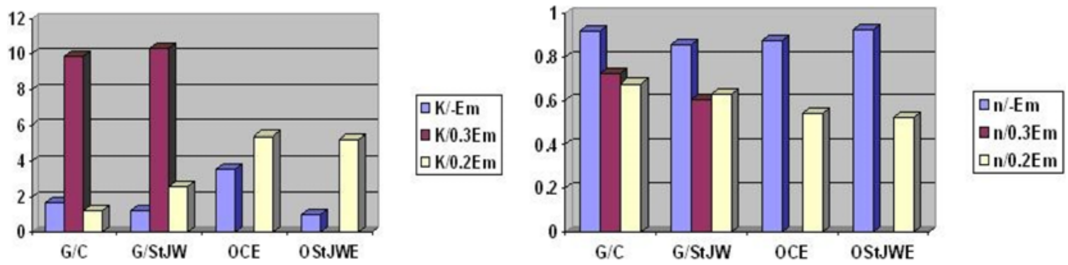


Fig. 3. Effect of the emulsifier on the rheological parameters: 3a - on the consistency index; 3b 0 on the flow index.

Table 2. Rheological parameters of compositions studied

Comp. no	K, Pa·s^n	n, –	Comp. no	K, Pa·s^n	n, –
1.0	0.5104	0.9927	1.18	0.6848	0.9133
1.1	0.869	0.9093	1.19	1.0313	0.9243
1.2	1.6611	0.9191	1.20	5.2217	0.5211
1.3	9.8554	0.7219	1.21	5.6472	0.5445
1.4	1.2218	0.6758	1.22	5.0087	0.5761
1.5	1.3574	0.6687	1.23	0.6903	0.9192
1.6	1.0716	0.6554	1.24	0.9634	0.9017
1.7	0.8197	0.8939	1.25	0.987	0.9141
1.8	1.2341	0.8553	1.26	0.8249	0.914
1.9	10.315	0.6019	1.27	0.7663	0.9136
1.10	2.5538	0.6315	1.28	1.0121	0.8656
1.11	2.6033	0.6281	1.29	0.6552	0.8603
1.12	2.4403	0.6352	1.30	0.791	0.9367
1.13	1.5548	0.894	1.31	0.5747	0.5979
1.14	3.5743	0.8694	1.32	1.8485	0.8819
1.15	5.4017	0.5421	1.33	0.6481	0.6572
1.16	6.9324	0.462	1.34	0.339	0.5817
1.17	5.3866	0.5627	1.35	1.0597	0.892

The UV screen (TiO_2) addition even in the tiny quantity of 0.2% mass was found to increase seriously the consistency of the compositions (almost twice-see 1.1-1.2 and 1.13-1.14 pairs of compositions) and to leave the flow index almost unchanged (or slightly decreased). Following the formulation path ETD Carbopol 2050 was added as emulsifier. Its addition in quantity of 0.3% mass to 10% PVA-in-water solutions containing 5% of glycerol plant extracts leads to drastic increase in consistency and decrease in the flow indexes (Table 2 - compositions 1.2 compared with 1.3 and 1.4). For the case of solutions containing olive oil plant extracts, the compositions became too consistent, hardly spreading on the skin, so the PVA concentration was decreased, and the emulsifier one was diminished from 0.3% mass to 0.2% mass (compositions 1.4, 1.10, 1.15 and 1.20 in Fig. 3). The experiments were carried out in pH range between 5.5 and 7.5 (the range of interest for pharmaceutics and cosmetics). For this range in the literature exists information of shear thinning behavior of ETD Carbopol 2050 solutions [4] which does not depend on the degree of neutralization in this pH interval. From the data in Table 2 and Fig. 3 it could be seen that the emulsifier's addition thickens drastically the compositions (the consistency index increasing about six times for the glycerol-containing compositions; the flow index in the same time decreases with 30%). On the other side, the addition of the preservative (Bronopol) almost does not affect the rheological parameters for the compositions containing glycerol extracts of calendula (1.4-1.5). For the compositions containing olive oil extracts of calendula the Bronopol addition leads to 28% increase in the consistency and about 15% decrease of the flow index (samples 1.15-1.16). The fragrance addition in EtOH solution in a quantity of 0.02% lowers the composition's apparent viscosity for the both solvents (K $\downarrow$, n $\uparrow$) - compare compositions 1.5 to 1.6 and 1.16 to 1.17. This influence is more pronounced for the case of the olive-oil containing compositions of calendula (compositions 1.16/1.17 - Table 2). The evident explanation of this fact is in the chemical formula of the solvent. For the case of the tutsan extracts, the influence of the fragrance is the same, but not so pronounced.

Microscopic observations showed that all emulsions studied (compositions, containing olive oil extracts) could be considered as highly flocculated systems. Fig. 4 shows two different emulsions where the presence of clusters of droplets is noticeable. A possible explanation of these aggregations could be the presence of individual non-adsorbing molecules.

Another set of experiments was carried out to elucidate the rheological behavior of sun-protection compositions with use of synthetic sun-protection components and of combination of natural and synthetic UV-absorbers and TiO_2 as UV-screen. The data of the com-

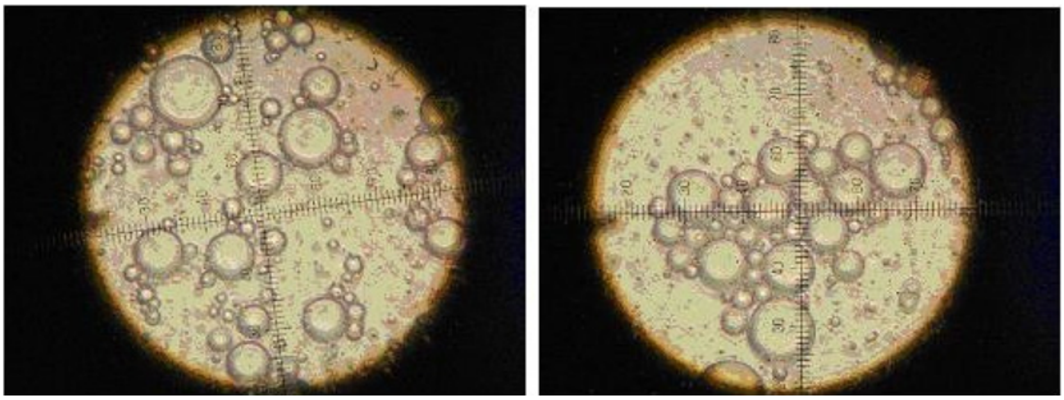


Fig. 4. Microscopic picture for the cosmetic sun-protection emulsions with olive oil extract of calendula (a) and tutsan (b).

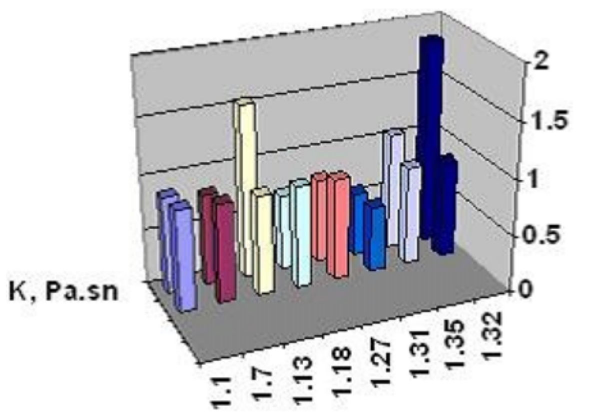


Fig. 5. Effect of the UV absorbers on the rheological parameters.

positions and their rheological parameters are summarized in Tables 1 and 2. From the data presented there the following conclusions can be derived:

- Fig. 5 shows no sensible effect of cinnamic acid addition in quantity of 1% mass on the flow index n (it decreases about 8%), (Table 1, compositions 1.27 and 1.28). Their consistency index increases about 50%. On the other hand, its addition together with 2,4 DHBPh leads to almost 3.5 times increase in K value and about 12% decrease of n (sample 1.32). So, evidently the influence of 2,4 DHBPh is quite stronger expressed, than that of the cinnamic acid. This fact is proved also by sample 1.35. As it was already reported [11,13] the simultaneous addition of olive oil and the glycerol extracts of calendula leads to drastic decrease in the consistency index of the compositions (about 4 times). Nevertheless, their addition together with 0.2% of 2,4 DHBPh does not affect much the flow index and lowers the consistency just about 40%.

- As it could be supposed, the addition of fine TiO_2 as UV-screen even in quite tiny quantity of 0.2% mass increases the consistency of basic 10% PVA samples, lowering in the same time the flow index n (see Table 2, samples 1.27, 1.28; 1.0, 1.30).

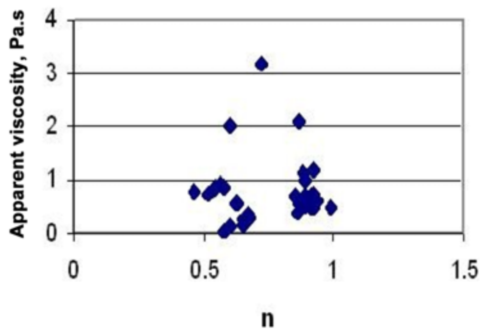
- If another UV-absorber - octylmethoxycinnamat is used in composition containing TiO_2, the effect is an opposite - K decreases, n remains almost unchanged, so a certain dilution of the composition is observed, without serious change in its pseudoplasticity (samples 1.28, 1.29). The same effect was noticed for the compositions with cinnamic acid and 2,4 DHBPh with TiO_2 (1.32, 1.33).

- A combination of two UV-absorbers and UV-screen was also studied: 2,4 DHBPh and cinnamic acid as UV-absorbers and TiO_2 - as UV-screen. Comparing samples 1.0 and 1.31 we observe a strong influence of 2,4 DHBPh on the flow index n - it decreases about 40%, thus increasing the pseudoplasticity of the compositions. The addition to this formulation of cinnamic acid (sample 1.32) increases the consistency index almost three times, increasing in the same time the flow index n. In this case the UV-screen addition to the compositions decreases K (just in the contrary to the cases already commented) but increases the pseudoplasticity with flow index n decrease - sample 1.33. So we can conclude that 2,4 DHBPh is governing composition in the flow behavior of these samples. If just 2,4 DHBPh presents in the samples (without cinnamic acid) the consistency index decreases and the flow index rests almost unchanged.

- A formulation containing 2,4 DHBPh and natural plant extracts was also studied (1.35). It contains equal quantities of glycerol and olive oil extracts of calendula. In this case the addition of these extracts thickens almost twice the formulation (sample 1.31 compared to 1.35).

Some compositions containing lavender oil and synthetic sun-protection components were also created (1.23 to 1.26). As it can be seen in Table 2 all of them are very slightly pseudoplastic with flow index values of about 0.91. It is evident that the lavender oil plays the governing role for the rheology, so the addition of the UV-absorbers and UV-screen quite slightly influences the product's properties. On the other hand, the lavender oil reappears in different market products as an aroma therapy component.

The dependence of the rheological parameters on the apparent viscosity is presented in Fig. 6. It is evident that for shear rate value of $\dot{\gamma}=60\ s^{-1}$ (shear rate of spreading on the skin) the apparent viscosity values are about 3-4 Pa·s for the samples 1.3 and 1.9. The relationship between the μ_{app} and the consistency index K for all the samples clearly exhibit two curves: the lower - with 5 mass % of PVA and the glycerol extracts; and the higher one - with 10 mass % and the olive oil ones. Almost the same observation could be made for the apparent viscosity dependence on the flow index n. As it was already noted, the 10% PVA solutions with olive oil plant extracts and preservative became too consistent to be spread, so in that case the 5% solutions were applied. Some of the compositions, especially with the synthetic sun-protection components exhibited quite low μ_{app}



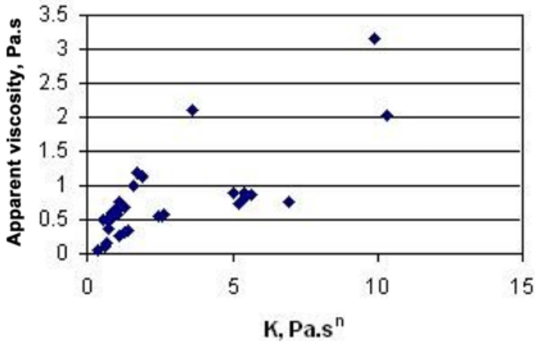


Fig. 6. Dependence of the apparent viscosities of the compositions at $\dot{\gamma}$=60 s^{-1} on the power-law model rheological parameters.

values. So, to provide higher viscosities some additional thickener is to be used. The dependencies of the apparent viscosity on the power-law model rheological parameters presented in the Fig. 6 cover quite wide range of values. So, they could be used in practice to obtain a composition with desired rheological behavior.

It was found that the compositions containing glycerol extracts are more stable than those with olive oil extracts, and they preserve their properties during at least six months. This fact could be explained by flocculating of the emulsions, presented in microscopic pictures.

The data presented can be used in equipment calculations for sun-protection formulations.

CONCLUSIONS

The rheological behavior of model cosmetic compositions based on polyvinylalcohol solutions and containing natural plant extracts in glycerol and olive oil, UV screens (TiO_2), synthetic UV absorber, emulsifier (Carbopol 2050), preservative (Bronopol) and fragrance was studied. The aim of the present work was the follow the mutual influence of these additives on the product flow properties. Their rheological properties during formulation were studied using co-axial cylinder viscometer. It was found that all the compositions are shear thinning and their rheological behavior can be described by the power-law rheological model. The emulsifier's addition thickens drastically the compositions (the consistency index increasing about 6 times for the glycerol-containing compositions; the flow index in the same time decreases with 30%). On the other side, the addition of the preservative (Bronopol) almost does not affect the rheological parameters, but leads to slight degree of thixotropy. The fragrance addition in EtOH solution, even in quite low quantities, lowers the composition's apparent viscosity (K ↓, n ↑). This influence is more pronounced for the case of the olive-oil containing compositions.

Microscopic observations showed that all emulsions studied (compositions, containing olive oil extracts) could be considered as highly flocculated systems where the presence of clusters of droplets is noticeable. A possible explanation of these aggregations could be the presence of individual non-adsorbing molecules.

The addition of fine TiO_2 as UV-screen, even in quite tiny quantity of 0.2% mass, increases the consistency of basic 10% PVA samples, lowering in the same time the flow index n.

It was also found that the compositions containing glycerol extracts are more stable than those with olive oil extracts and they preserve their properties during six months.

The data obtained can be used for creating cosmetic compositions with desired rheological properties and in calculations of equipment for cosmetic formulations.

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NOMENCLATURE

τ : shear stress [Pa]
K : consistency index [Pa·s^n]
$\dot{\gamma}$: shear rate [s^{-1}]
n : flow index [-]
μ_{app} : apparent viscosity [Pa·s]

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