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Rheological behavior and the SPF of sunscreens

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Abstract

Due to a large variety of sunscreens, it is important to study among other things, the effect of the vehicle on the thickness and uniformity of sunscreen films. In this study, we determined the physical stability of five sunscreens SPF 15 (FA to FG), containing or not PVP/eicosene crosspolymer (PVP/EC), and two different self-emulsifying bases (SEB), and also evaluated the influence of the vehicle in their SPF. In the study of physical stability, formulations were stored at 25, 37 and 45 °C, for 28 days. Viscosity and rheological behavior of the formulations were determined using a Brookfield rheometer. Investigations of the SPF were carried out in a group of 30 volunteers (COLIPA methodology). The FC samples (phosphate-based SEB), with a lower thixotropy, showed statistically higher SPF (13.6) when compared with FB (non-ionic SEB), which presented higher thixotropy and a SPF of 9.84. The FE sample (phosphate-based SEB+PVP/EC) presented the same SPF as the FC, but had a higher thixotropy. The FB formulation (stable with higher thixotropy) showed the lowest SPF while FC (an unstable formulation with lower thixotropy) presented a higher SPF. We concluded that FE was the best formulation showing a higher SPF and stability and the study of rheology can help the development of sunscreens.

Keywords: Sunscreens; Rheology; Thixotropy; SPF; Stability

1. Introduction

The recent rapid growth of sunscreens' marketing indicates that even though a suntan is still desired, people are nevertheless quite conscious of accompanying dangers like actinic changes (wrinkling, premature ageing of the skin, irregular thinning of the epidermis, hyperpigmented macules), development of premalignancies (solar keratoses) and skin cancer (melanomas, basal and squamous cell carcinomas) occurring as a result of excessive exposure to ultraviolet (UV) radiation (Pathak and Fitzpatrick, 1993).

With the massive introduction of sunscreening active agents into a large variety of functional products, it is more than ever necessary for the cosmetic chemist to better know the chemical structure and the reactivity of chemicals used, their potential interaction and effect on cosmetic formulations (Shaath, 1986; Hewitt, 1999).

Despite the fact that many aspects of cosmetic chemistry still remain an art, in the area of the sunscreens a better understanding of physicochem-

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ical principles (Shaath, 1986), as well as the factors related to the application technique and type of sunscreen applied are necessary to achieve the required goals (Diffey, 2001).

There are many examples of formulations that do not exhibit an increase in sun protection factor (SPF) by increasing the levels of sunscreen actives. Thus, it is clear that several other factors must be considered when formulating sunscreen products including film thickness, uniformity (related to rheology) and opacity. None of the above parameters, however, addresses the chemistry of sunscreens (Dahms, 1994a; O'Neil, 1984; Shaath et al., 1992; Wünsch, 2000).

At present, the cosmetic industry is using antioxidants like vitamins (Krol et al., 2000) and enzymes (Krutmann, 2001) as additions to UV filters, because almost all the postradiation reactions involve directly or not, reactive oxygen species (ROS). One of the vitamins used is vitamin E, the most important lipid-soluble membrane-bound antioxidant in the body, which provides protection against DNA inactivation as well as cell damage (Ragarajan and Zatz, 1999; Idson, 1993). Although this association provides many benefits, it can also cause instability of sunscreen formulations.

This way, it is important to determine the stability of this kind of cosmetic product. There are some studies that have reported the chemical stability of vitamins or UV filters in cosmetics (Gallarate et al., 1999; Kim and Lee, 1999; Marti Mestres et al., 1997) however, there are few studies about the physical stability of sunscreens supplemented with vitamins.

The objectives of the present study were to determine the physical stability of five sunscreen formulations (FA to FG, containing or not PVP/eicosene crosspolymer (EC) and two different self emulsifying bases), with ethylhexyl methoxycinnamate 7%, benzophenone-3 2% and ethylhexyl salicylate 0.5%, and to evaluate the influence of the vehicle (mainly the thixotropy) on their SPF. It was also proposed to evaluate the best vehicle to be supplemented with 5% vitamin E acetate (VEA).

2. Materials and methods

2.1. Formulations studied

Five formulations (Table 1) were prepared in a Heidolph RZR 2021 shaker at approximately 625 rpm, and supplemented or not with 5% VEA. Formulations FB, FC, FD and FE, which are shown in Table 1, also contained the sunscreens ethylhexyl methoxycinnamate 7% (UVB), benzophenone-3 2% (UVA) and ethylhexyl salicylate 0.5% (UVB). Formulation A also contained 7.5% of a blend of hydrophilic sunscreens benzophenone-4 (UVA) and phenylbenzimidazole sulfonic acid (UVB).

2.2. Determination of the rheology of the formulations

Samples of the five formulations were stored at room temperature, 37 and 45 °C, for a period of 28 days. The viscosity and rheologic behavior of the formulations were determined at 7-day intervals during this period, using a Brookfield Cone and Plate type rheometer, model DV-III. A Brookfield software program, RHEOCALC version V 1.01 was also used.

Rheograms and viscosity measurements were made under the following experimental conditions: 25 °C, 0.5 g samples and CP52 spindle. To obtain the ascendant curve, rotation speeds were progressively higher (10–58 rpm) and the procedure was repeated in reverse with gradually decreasing speeds (58–10 rpm) for the descendant segment.

The rheograms obtained were mathematically analyzed by the Ostwald Law, where values of apparent viscosity and flow index (related to the degree of sample pseudoplasticity) were obtained.

The numeric integration of the rheogram curves was made by the Software MICROCAL ORIGIN and the area under the ascendant and descendant curves was obtained (loop area hysteresis-thixotropy).

Viscosity, flow index and thixotropy ratios among values obtained in different times during the test and the initial value were calculated to observe the rheological behavior of the formulations studied.

Table 1
Components of the formulations under study

Formulations					
Components	Percentage of components in each formulation				
	FA	FB	FC	FD	FE
Non-ionic self-emulsifying base (cetearyl alcohol and ceteareth-20)	–	6.00	–	–	–
Phosphate-based self-emulsifying base (cetearyl alcohol, dicetyl phosphate, ceteth-10 phosphate)	–	–	5.00	4.00	5.00
Ceteareth-20	–	3.00	–	–	–
Lanolin derivatives	–	9.00	–	–	–
Glycerin 86%	–	5.00	–	–	–
Propyleneglycol	5.00	–	3.00	3.00	3.00
Phenoxyethanol and methylparaben, ethylparaben, propylparaben and buthylparaben	0.8	0.8	0.8	0.8	0.8
BHT	0.05	0.05	0.05	0.05	0.05
Carbomer	1.00	–	–	–	–
Neutralizing agent	qs.	qs.	qs.	qs.	qs.
Polimeric emulsifier (acrylate/C10-30 alkyl acrylate crosspolymer)	–	0.24	0.2	0.2	0.2
Silicone microemulsion	2.00	–	–	–	–
Hidrogenated and etoxillated castor oil 40 OE	–	–	0.2	0.2	0.2
Volatile silicone	–	–	2.0	2.0	2.0
PVP/EC	–	–	–	1.0	1.0
Shea butter	–	–	–	10.0	–
Distilled water qs. to	100.0	100.0	100.0	100.0	100.0

Viscosity, flow index and thixotropy data as well as their ratio values were analyzed using a non-parametric test, Kruskal–Wallis.

2.3. Determination of the SPF

The assessments of the SPFs of three formulations (B, C, E) were carried out on a group of 30 human volunteers aged between 18 and 50 years, with skin types I and II (determined according to ITA° values, individual typologic angles, which is a colorimetric prediction of Minimal Erythema Dose-MED), according to the COLIPA methodology, (The European Cosmetic Toiletry and Perfumery Association), using ten volunteers for each formulation.

Samples of formulations (2 mg/cm^2) were spread evenly on the untanned skin of the midback (25 cm^2). About 15 min later the areas were exposed to 25% increments of radiation from the solar simulator (UVA/UVB xenon arc lamp). The MED was determined 16–24 h later. The individual SPF was calculated as the ratio of MEDs in protected and unprotected skin, respectively. The SPF data were analyzed using a non-parametric test, Kruskal–Wallis.

3. Results and discussion

The apparent viscosities at the loop apex (116 per s), analyzed 24 h after preparation and storage of the formulations at room temperature are presented in Table 2. Formulations A (gel) and D showed statistically higher viscosity values than the others, and formulation C was statistically less consistent than the others ($P < 0.01$). The addition of VEA did not produce significant alterations in the viscosity of the formulations, only in formulation B the addition of VEA provoked a statistically significant viscosity enhancement ($P < 0.001$).

The results showed that the formulations had pseudoplastic behavior, with a flow index below 1 (Martin et al., 1993). The addition of VEA to formulations D and E produced significant altera-

Table 2
Apparent viscosity at the loop apex, flow index and hysteresis loop area values (thixotropy) for five different formulations, with or without addition of VEA, 24 h after preparation and storage at room temperature; and SPF values of formulation B, C and E using human volunteers

Formulations	Viscosity (cP)	Flow index	Thixotropy (dyne/cm^2 s)	SPF
Form A	1476±9	0.27±0.00	1510±760	–
Form A+VEA	1680±29	0.27±0.00	1156±436	
Form B	1017±61	0.25±0.02	25 597±117	9.84±1.64
Form B+VEA	1298±30	0.26±0.01	24 837±1523	–
Form C	836±16	0.26±0.01	1740±529	13.60±1.90
Form C+VEA	863±21	0.28±0.01	2925±886	–
Form D	1476±55	0.26±0.01	17 423±3121	–
Form D+VEA	1312±10	0.29±0.00	17 582±2053	–
Form E	1159±73	0.29±0.03	29 042±2450	13.60±1.58
Form E+VEA	1107±153	0.25±0.01	21 557±4437	–

tions in these flow index values (Table 2) after 24 h since their preparation ($P < 0.001$). Sunscreen formulations with a pseudoplastic flow produce a coherent protective film covering the skin surface with evenly distributed UV filters, and this activity is important for a higher SPF (Hewitt and Dahms, 1996). Newtonian materials do not behave in this way, because when spread on the skin they run very quickly, reducing the protective film (Dahms, 1994b). The pseudoplastic material, however, can break down for easy spreading, and the applied film can gain viscosity instantaneously to resist running (Pader, 1993).

Some hysteresis area (thixotropy), a pseudoplastic natural characteristic, were observed in the rheograms obtained (Fig. 1) and the presence of VEA did not alter the thixotropy of the formulations (Table 2). Formulations A and C had statistically lower thixotropy values than the other formulations ($P < 0.001$) due to the characteristics of formulations raw material. The presence of consistency agents (cetearyl alcohol) and rheological additives (PVP/EC) in the formulations B, D and E provoked an enhancement of thixotropy values (Clarke, 1993).

The addition of PVP/EC and shea butter to formulation D, produced peaks in the rheograms curves, specially when the formulation was supplemented with VEA, this being considered as an instability signal (Fig. 1C).

Figs. 2–4 present the ratios between values (viscosity, flow index and thixotropy) obtained in different times during the test and the initial value, showing the alterations in formulation that took place during the experimental period.

Formulations A, B and D presented oscillations in the viscosity parameter (Fig. 2). These oscillations were more pronounced for formulation D when stored at room temperature, due to the shea butter rheological characteristic. These oscillations did not occur when VEA was present, probably due to the interaction with VEA and unsaturated fatty acids presented in shea butter (Idson, 1993). Formulation A, supplemented or not with VEA had more pronounced alterations when it was stored at 37 and 45 °C. Formulation B had its viscosity decreased mainly when it was stored at 37 °C (without VEA) and 45 °C (with VEA). In this case, the amount of consistency agent was probably not enough to keep the viscosity of the formulation constant during the stress conditions applied in this physical stability study (Miner, 1993).

The flow index values decreased when formulations A, B and D were stored at room temperature, 37 and 45 °C during the test, and in the presence of VEA these alterations were more pronounced for formulation A, when stored at 45 °C (Fig. 3E and F) and for formulation D, when stored at room temperature and 45 °C, (Fig. 3A, B, F) due to the composition of these formulations. Formulation E showed a statistically significant increase in flow index value on the seventh day of the test, when stored at room temperature, ($P <$

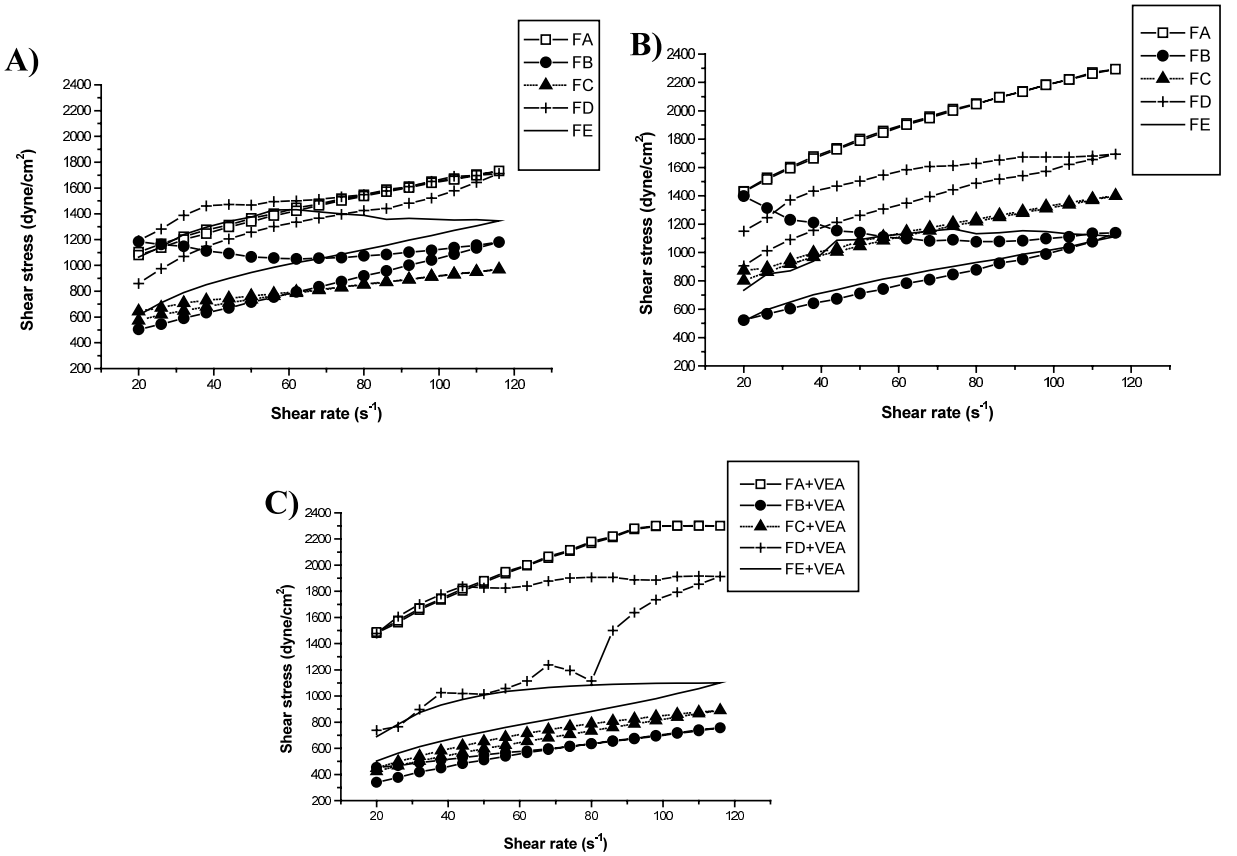

Fig. 1. Rheograms of formulations FA, FB, FC, FD and FE (A) formulations stored at room temperature, 24 h after preparation; (B) formulations stored at 45 °C, 28 days after preparation; (C) formulations supplemented with VEA stored at 45 °C, 28 days after preparation.

0.001), which was kept constant during the remaining experimental period (Fig. 3A).

Consequently, this formulation needs about 7 days to organize its structure and become stable.

The addition of PVP/EC to formulation C (formulation E) enhanced the thixotropy value to 29042 dyne/cm^2 s ($P < 0.001$) and also the stability. At room temperature and at 45 °C, formulation C showed very low thixotropy values (Fig. 4A). The addition of VEA, also increased the thixotropy values but they were reduced again at the end of the test (28 days stored at 45 °C) (Fig. 4F). Formulation A was unstable when supplemented with VEA, and stored at room temperature, 37 and 45 °C, which can be seen in Fig. 4B, D, E. On the same way, Formulation D was unstable when supplemented with VEA, and stored at room temperature and 45 °C, as can be seen in Fig. 4B and F, with the enhancement of thixotropy at room temperature and at 45 °C. Formulations that keep pseudoplastic flow and high thixotropy values constant during the storage period has been considered stable, because when the system is disorganized, it takes time to reorganize its structure (Miner, 1993).

In summary, the results show that formulations FB (non-ionic self-emulsifying base) and FE (phosphate-based self-emulsifying base + PVP/EC) presented higher thixotropy values (25 597 and 29 042 dyne/cm^2, respectively) (Table 2), and were stable, however, formulation FE stability was higher (Fig. 2). Formulation FC (phosphate-based self-emulsifying base) showed lower thixotropy (1740 dynes/cm^2) and was unstable. Formulations

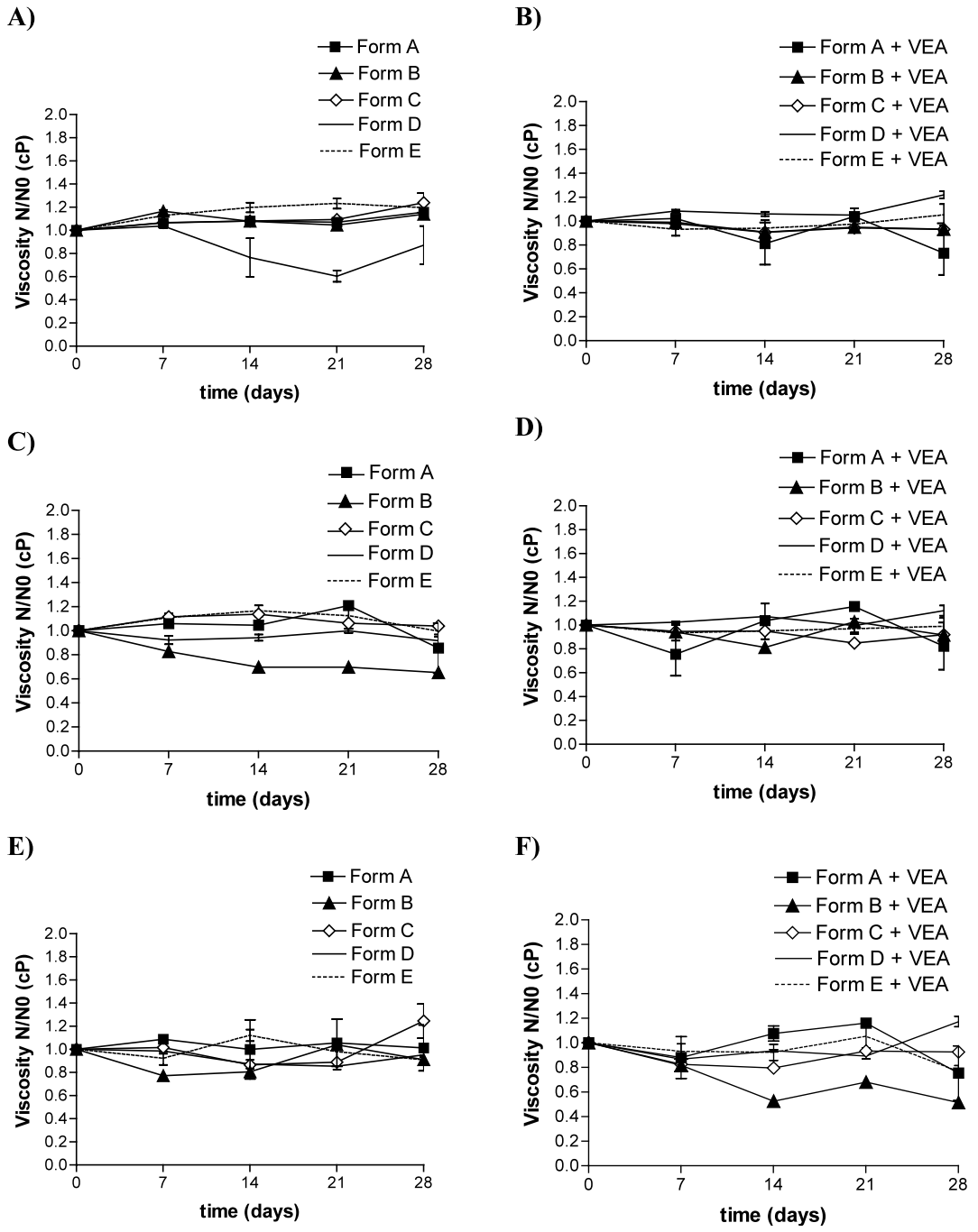

Fig. 2. Alterations in the viscosity of formulations during the experimental period. Viscosity values are ratios between values obtained during the test at different times and the initial one. (A) Formulations stored at room temperature; (B) formulations supplemented with VEA stored at room temperature; (C) formulations stored at 37 °C; (D) formulations supplemented with VEA stored at 37 °C; (E) formulations stored at 45 °C; (F) formulations supplemented with VEA stored at 45 °C.

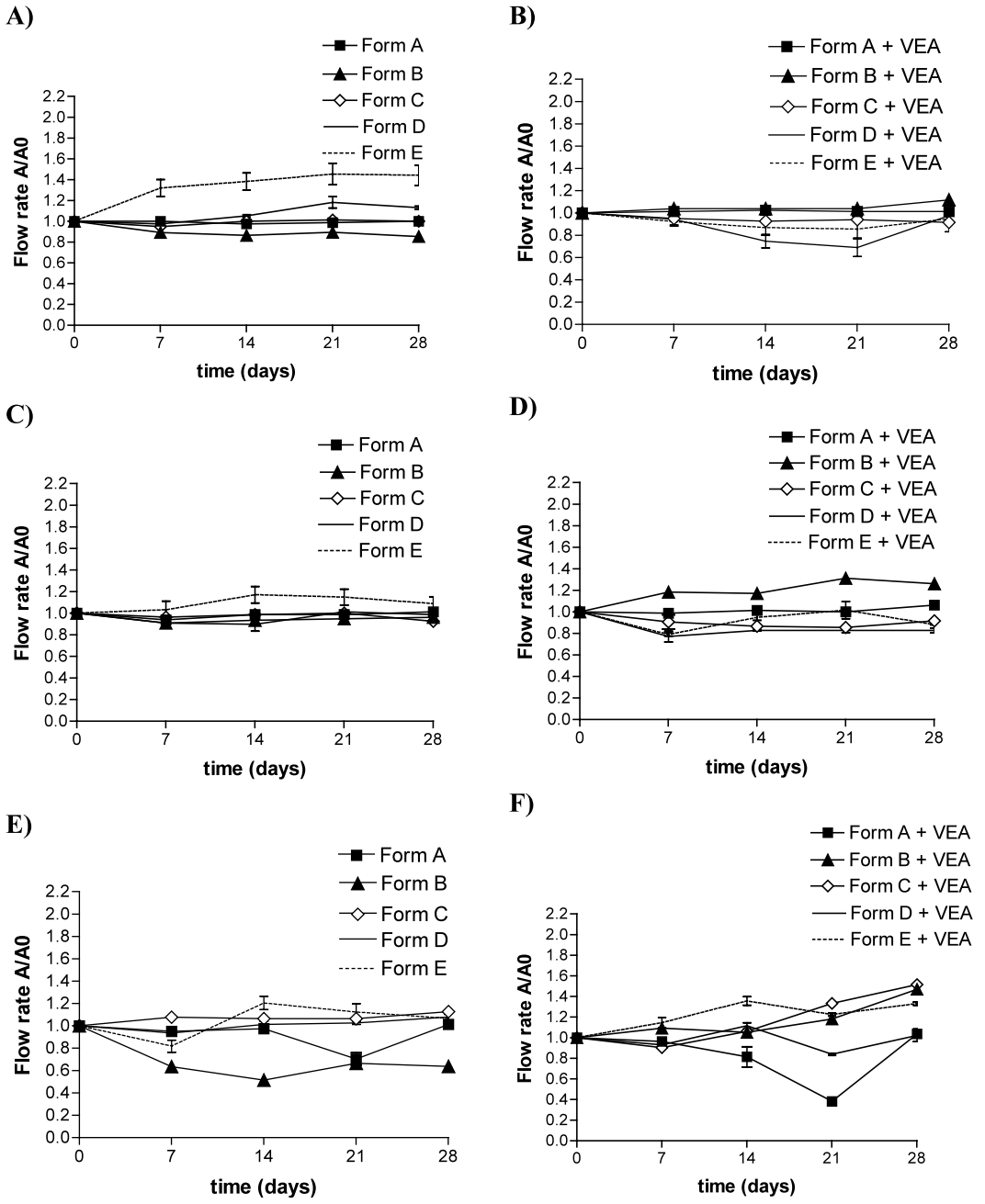

Fig. 3. Alterations in the formulations flow index during the experimental period. Flow index values are ratios between the flow index at different times during the test and the initial value. (A) Formulations stored at room temperature; (B) formulations supplemented with VEA stored at room temperature; (C) formulations stored at 37 °C; (D) formulations supplemented with VEA stored at 37 °C; (E) formulations stored at 45 °C; (F) formulations supplemented with VEA stored at 45 °C.

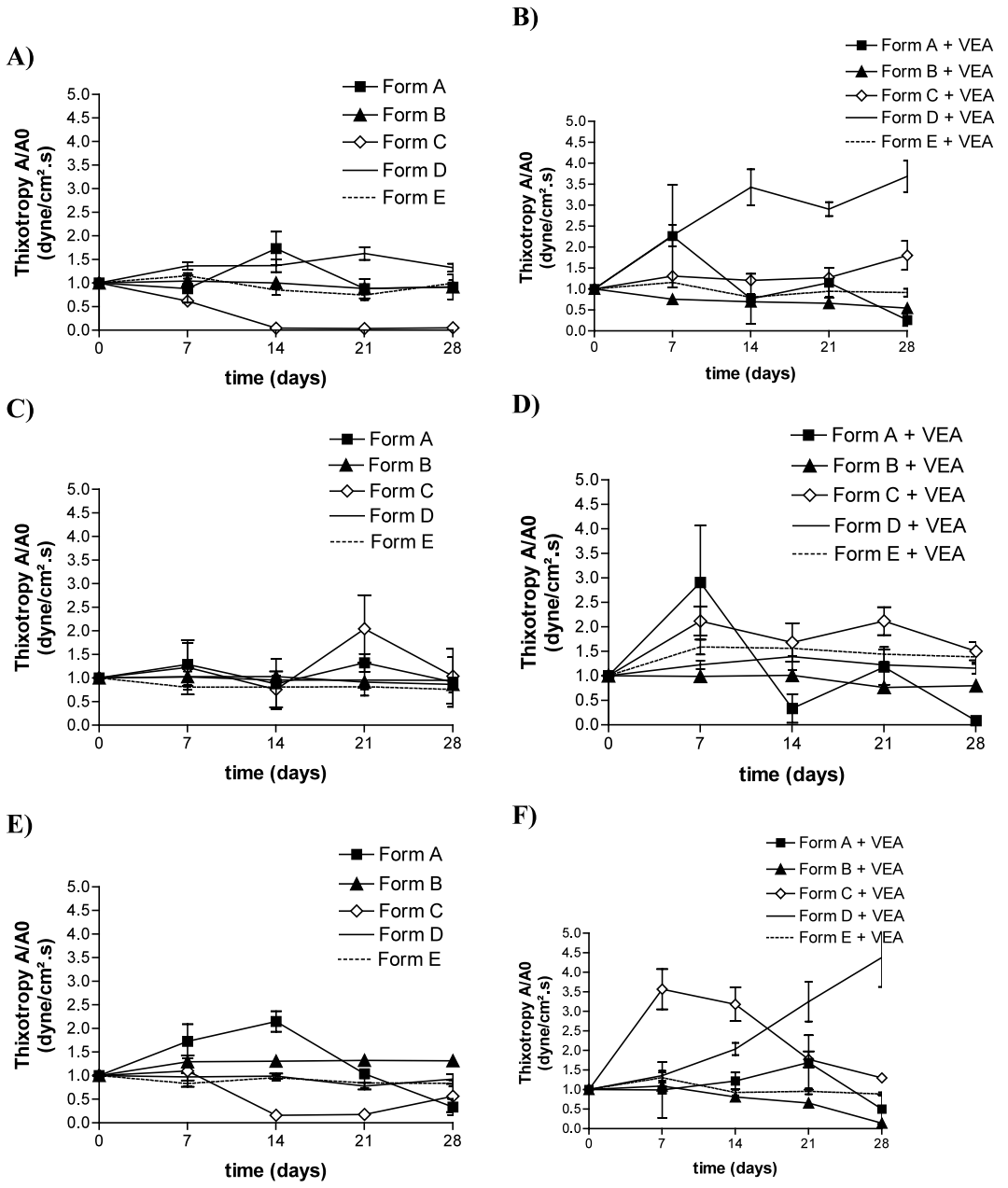

Fig. 4. Alterations in the thixotropy of formulations during the experimental period. Thixotropy values are ratios between values at different times during the test and the initial ones. (A) Formulations stored at room temperature; (B) formulations supplemented with VEA stored at room temperature; (C) formulations stored at 37 °C; (D) formulations supplemented with VEA stored at 37 °C; (E) formulations stored at 45 °C; (F) formulations supplemented with VEA stored at 45 °C.

FA (carbomer based) and FD (phosphate-based self-emulsifying base + PVP/EC + shea butter) were unstable showing alterations in viscosity, thixotropy and flow index (Figs. 2–4). Hence, the formulation E presented the most constant rheological characteristics, when viscosity, flow index

and thixotropy were analyzed and compared with the other formulations.

3.1. SPF determination

This test was carried out with three formulations: FB and FE, which were more stable than the others and FC, which showed lower thixotropy, to determinate the influence of thixotropy on the SPF.

The SPF values determined for three formulations (B, C, E) are presented in Table 2.

Statistical analysis showed that SPF values for FC and FE were not significantly different, but FB was statistically different from FC and FE ($P < 0.001$).

Relating thixotropy to SPF values, it can be seen the FC, with a lower thixotropy, showed a statistically higher SPF (13.6) ($P < 0.001$) when compared with FB, with higher thixotropy and SPF (9.84). Formulation FE containing PVP/EC, showed higher thixotropy, but had the same SPF as FC.

Rheological behavior has a fundamental importance in the formulation of sunscreens, because the formation of an evenly distributed film is critically influenced by the flowing properties of the formulation. Dahms (1994b) studied the effects of thixotropy on the UV absorption of sunscreen emulsion formulations, using an instrument described by Diffey and Robson (1989) to compare the in vitro SPF values, and it was noted that optimum protection of the skin is only possible when the preparation covers the complete area of skin to be protected. In the ideal case, the complete skin relief is covered with an even layer thickness. Therefore, the UV protection effect of an emulsion on the skin is also a function of emulsion rheology.

In a further study, Hewitt and Dahms (1996) compared the SPF values determined in vitro (using an instrument described by Diffey and Robson, 1989) and in vivo (using five human volunteers as described by FDA and COLIPA) methodologies, and showed that there was no significant difference between the values. They also indicated that some rheological additives, used to alter the thixotropy and recovery time of the emulsions after high shear rates, influenced the SPF of the sunscreens studied.

There is an optimal value for thixotropy in order to achieve the highest possible SPF. With lower values, the spreadability is insufficient to permit good distribution of the sunscreen. Above the optimum thixotropy, there is insufficient recovery of the structure to give a product with a film evenly distributed, as it continues to flow into the wrinkles of the skin (Hewitt and Dahms, 1996).

Dahms (1994b) showed that emulsions that have high thixotropy values present lower SPF values. Thus, ideal formulations would be the ones that present lower thixotropy (formulations FA and FC). However, FA is stable only when it contains hydrosoluble UV filters, which have lower resistance to washing-off. Kaidbey and Klingman (1981) demonstrated that formulations containing benzophenone-4 (sulisobenzone), submitted to a wash-off test, was completely washed-off after 40 min. Also FA was unstable when supplemented with VEA.

Formulation FC showed lower thixotropy values at the beginning of the test, but during the experiment there was an enhancement of this value, indicating instability; according to Dahms (1994b) an increase in thixotropy during storage of a sunscreen compromizes its efficacy due to SPF reduction.

Under the present experimental conditions, we observed that FB (a stable formulation with higher thixotropy) presented the lowest SPF. FC (an unstable formulation with lower thixotropy) presented a higher SPF. Therefore, both formulations do not offer the desired performances for commercial purposes. Thus, formulation FE was the best one since it presented a higher SPF and stability.

On the other hand, the PVP/EC enhanced the thixotropy values and stability of FE, but did not alter the SPF, since FE and FC (without this polymer) had the same SPF. Therefore, the composition of the formulations and the characteristics of the raw materials used, which were detected in this study by the rheological behavior, influenced the SPF, since formulations FB and FC had the same UV filters at the same concentration, and showed statistically different SPF values.

Thus, it seems that SPFs of the sunscreen formulations depended on rheological behavior. Considering this parameter FE was the best formulation. Since the effect of sunscreens have been dependent on their rheological behavior, the study of rheology can help the development of a simple quick and cheap screening method for this category of cosmetic products.

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