

PABA-ALGINATE COMPLEX AS SUNSCREEN AGENT

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Summary

In order to improve the photostability of p-aminobenzoic acid as UV-B sunscreen agent, an electrostatic complex with sodium alginate was formed. The occurring of the complex formation was demonstrated by rheological analysis and by difference spectrophotometry. Photodegradation of PABA and PABA-alginate complex, resulting from irradiation by sunlamp, was examined by UV spectrophotometry. The complex showed a greater UV absorbance capacity and nearly overlapped photodecomposition rate in comparison with the original sunscreen agent.

Riassunto

Per migliorare la fotostabilità dell'acido para-aminobenzoico (PABA) utilizzato come filtro UV-B, è stato preparato un complesso di natura elettrostatica con il sodio alginato. La formazione del complesso è stata dimostrata mediante misure di reologia e di spettrofotometria differenziale. La fotodegradazione del PABA e del complesso PABA-alginato, dovuta all'esposizione a raggi ultravioletti, è stata valutata mediante misure spettrofotometriche UV. Il complesso ha mostrato una aumentata capacità filtrante pur mantenendo una velocità di fotodecomposizione paragonabile a quella del composto come tale.

INTRODUCTION

The knowledge of sun exposure side-effects led recently to a growing interest in cosmetic products containing sunscreen agents. However, UV absorbance involving the sunscreen photodegradation (1) might have consequences in terms of photoprotection or phototoxicity (irritation, allergic or photoallergic contact dermatitis, carcinogenic risk).

One of the first and widely used UV-B absorbers is *p*-aminobenzoic acid (PABA). Published papers have reported that PABA decomposes by sun exposure and potentially harmful metabolites are formed, with also possible changes in screening efficiency. Nevertheless, there is some discrepancy between the reports (2-6).

Since the photochemical modification of PABA involves the amino group (6), the present work attempts to improve PABA photostability by forming a complex with alginate, a polyanionic polysaccharide. Alginates form gels by interacting with polyvalent cations and cationic compounds for which mannuronic residues are mainly involved (7-9).

Therefore, the occurring of the complex formation between PABA and sodium alginate as well as the photodegradation after UV irradiation were tested by monitoring the rheological and UV spectral changes.

MATERIALS AND METHODS

Materials

The following chemicals were obtained from commercial suppliers and used without further purification. Sodium alginate Manucol DM (Mr about 147000, extracted from *Laminaria digitata*, containing 62% mannuronic acid and 38% guluronic acid) was kindly supplied by Kelco International (Bagnolet Cedex, France). *p*-aminobenzoic acid (PABA) was purchased from

Fluka Chemie (Buchs, Switzerland).

Rheological analysis

Rheological measurements were carried out on 0.5% (w/v) solutions (water and acetic buffer solution at pH 3.5) of both sodium alginate alone and in the presence of increasing amounts of PABA such as to produce true solutions, i.e. without precipitate. After 24 h, the rheological behaviour of the solutions was determined at 25°C in a coaxial cylinder rheometer (Rotovisco RV 12, Haake, Karlsruhe, Germany) by measuring the shear stress as a function of the shear rate. The reported data represent the average of three determinations.

Difference Spectrophotometry

Difference Spectrophotometry (DS, UV-Vis Lambda 16, Perkin-Elmer, Norwalk, CT, USA) was performed by the Herskovit's double cell compensation technique (10). The baseline was set to zero with water and sodium alginate water solution (0.136 μ M), in double cells in both reference and sample beams. Difference spectra were recorded after addition of the same amount of PABA to water in the reference compartment and to sodium alginate water solution in the sample compartment obtaining increasing PABA concentrations up to 118 μ M. The absorbance of PABA in water (118 μ M, pH 5.9) and in alginate solution (0.136 μ M, pH 6.5) did not change.

Molar extinction coefficient determination

To evaluate the role of the complexation on PABA screening efficiency, the molar extinction coefficient was calculated on the absorbance values, at the maximum absorbance wavelength, of PABA water solutions with water as referen-

ce and of PABA-alginate water solutions with sodium alginate water solution as reference. The data represent the average of three differently concentrated solutions.

Evaluation of photodegradation

Solutions of 0.1 % (w/v) PABA in water and in 0.5 % (w/v) sodium alginate water solution were placed in standard quartz cuvettes (1 x 1 x 4 cm). The cuvettes were exposed to the radiation by a light source from 280 to 400 nm (HP 3115, Philips, Eindhoven, The Netherlands) at a distance of 25 cm and a temperature of 30°C by an air flow. After dilution to 29 μ M PABA concentration, UV spectra were recorded (Lambda 3B, Perkin-Elmer) every 15 min for 2 h with water or 0.5% w/v sodium alginate water solution as references.

RESULTS AND DISCUSSION

PABA-alginate complex evaluation

PABA-alginate complex formation was investigated by means rheological analysis and Diffe-

rence Spectrophotometry.

Rheological analysis. Unlike uncharged polymers, dilute solutions of polyelectrolytes show an "electroviscous effect" which leads to increased viscosities. This results from a spatial expansion of the hydrodynamic volume of the molecules due to electrostatic repulsions between charged segments subsequent to the dilution of the counter ion layer surrounding the molecules (11). A 0.5% (w/v) solution of sodium alginate is considered a dilute polyelectrolyte solution having an expanded configuration (12). In such conditions, the addition of a compound having a cationic group and able to interact with the polyanionic alginate decreases the intramolecular repulsion leading to a tighter configuration and, consequently, to a reduced viscosity. Therefore, rheological measurements were carried out on sodium alginate 0.5% (w/v) solutions in the presence of increasing amounts of PABA in order to determine the possible interaction between PABA and alginate.

The relative apparent viscosity obtained for a shear rate of 1385 s^{-1} (where 100% is considered the value of pure alginate) was plotted in function of PABA concentration (Fig. n. 1).

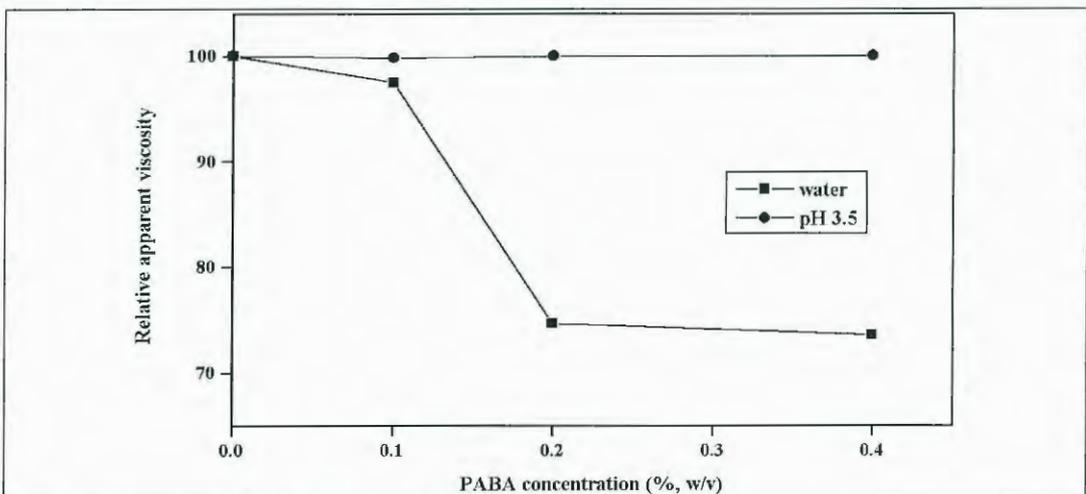


Fig. 1 Relative viscosity values of 0.5 % w/v alginate solutions at different PABA concentrations.

The presence of PABA led to a reduced viscosity of the alginate solution only in water, whereas no significant changes in viscosity were observed at pH 3.5. This finding suggests that the complexation involves an electrostatic interaction between dissociated PABA amino group and alginate carboxylic groups.

Difference Spectrophotometry. The binding between PABA and alginate was also evaluated by Difference Spectrophotometry, recording the absorbance spectra differences between solu-

tions of PABA alone and PABA-alginate mixtures. Each difference absorbance spectra was characterized by positive and negative peaks, as shown in Figure n. 2.

These appear at wavelengths differing from that of the maximum absorbance of the compound under study. A curve was then generated by plotting the change in absorbance (ΔA), measured as the difference in absorbance of the positive peak from the baseline, versus concentration of PABA added (Fig. n. 3)

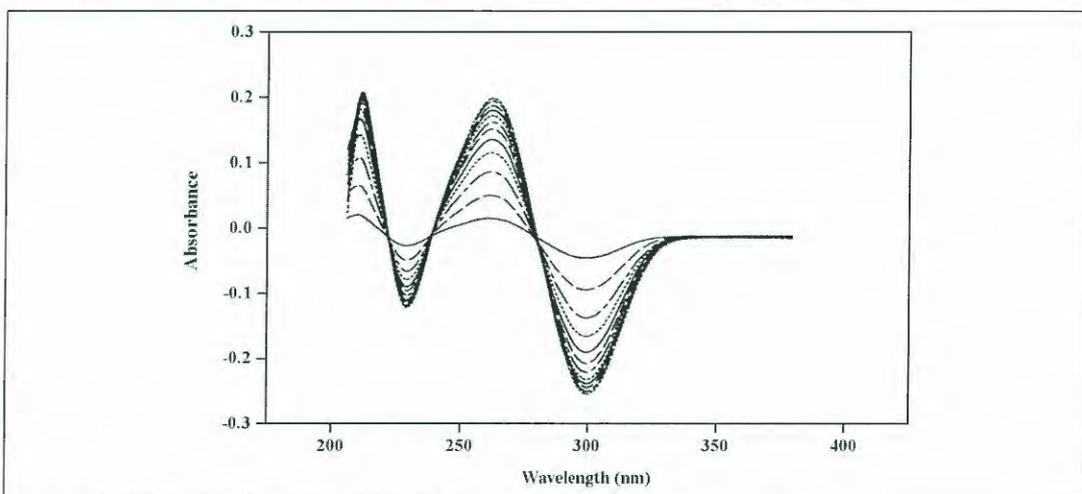


Fig. 2 UV spectra difference between PABA and PABA-alginate solutions obtained by Difference Spectrophotometry.

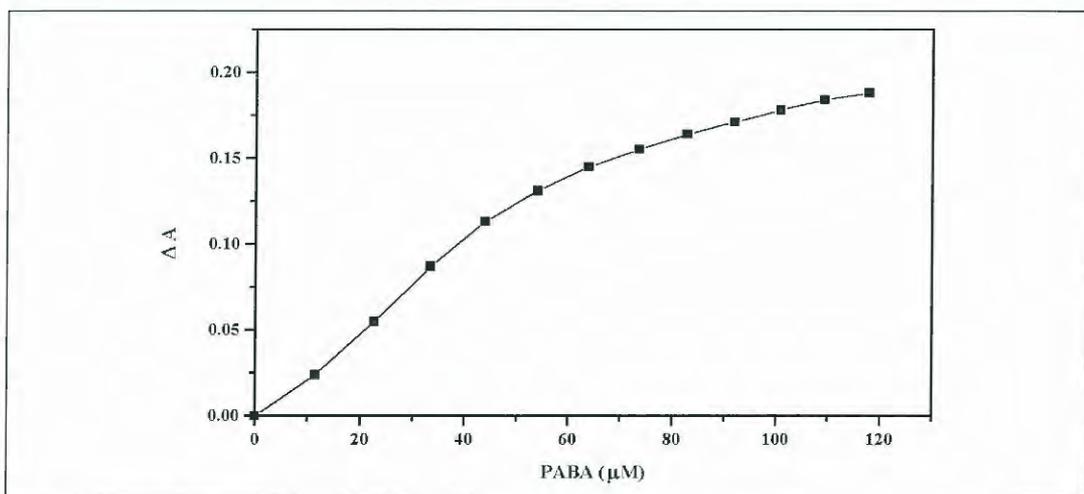


Fig. 3 Absorbance differences of PABA-alginate solutions as a function of PABA concentration.

ΔA increased along with PABA concentration value indicating the occurring of an interaction between PABA and alginate.

Photodegradation study. The UV spectra of both PABA and PABA complex obtained before irradiation are presented in Figure n. 4.

PABA complex showed a slight shift of the maximum absorbance wavelength, from 273 nm to 267 nm, in comparison with PABA and a substantial increase in absorbance values (the molar extinction coefficient was $21.37 \cdot 10^3$ at 267 nm for the PABA complex and $14.77 \cdot 10^3$ at 273 nm

for PABA). The observed phenomenon could not be attributed or affected by PABA ionization change in function of the different solution pH value. In fact, no variations in PABA molar extinction coefficient were observed between PABA in acetate buffer at pH 5.9 (pH value of 29 mM PABA water solution) and PABA in acetate buffer at pH 6.5 (pH value of 29 mM PABA in alginate water solution).

The spectral changes of PABA and PABA-alginate complex exposed between 0 and 2 h are shown in Figure n. 5.

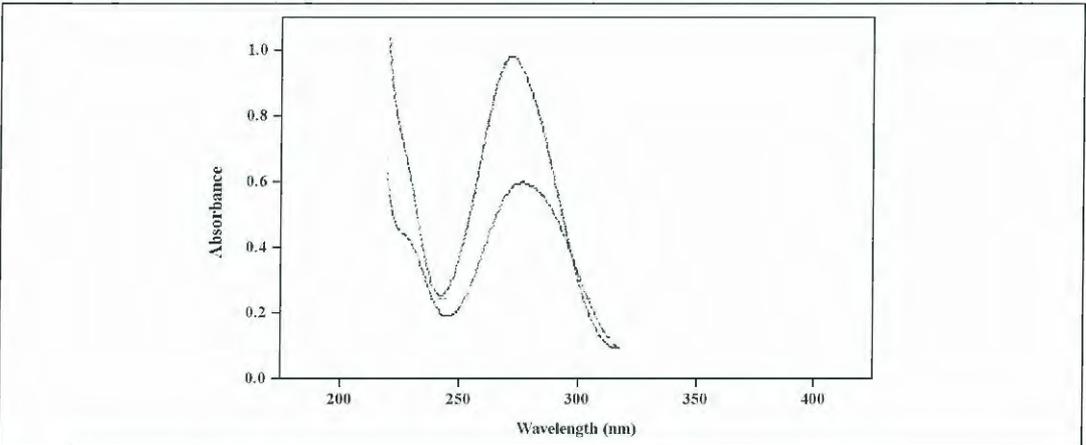


Fig. 4 UV spectra of PABA (lower line) and PABA-alginate (upper line).

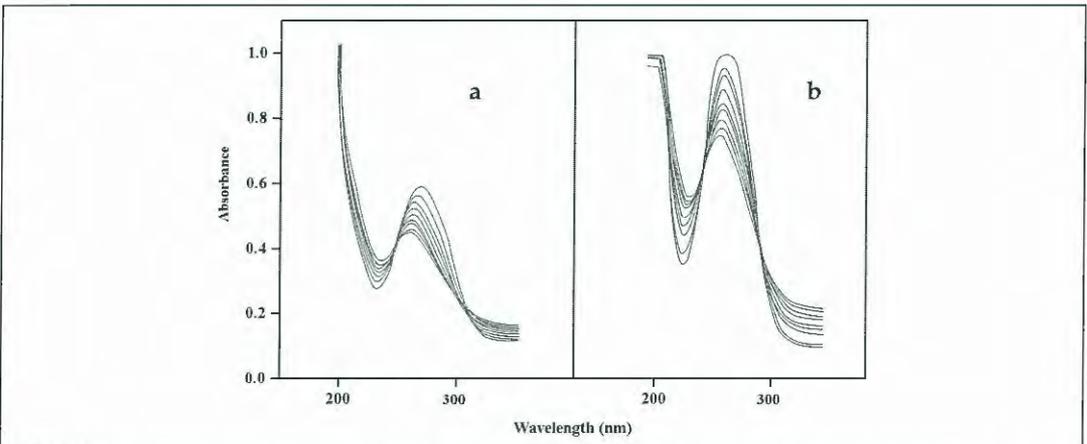


Fig. 5 Spectral changes of PABA (a) and PABA-alginate (b) exposed from 0 (top) to 2 h (bottom) to the solar simulator (tracings correspond respectively to 0, 15, 30, 45, 60, 75, 90, 105 and 120 min irradiation time).

The isosbestic points of the spectra are well defined indicating a single process: sunscreen \rightarrow photoproduct. After exposure, the absorbance values as well the maximum absorbance wavelength decreased along with the exposition time in both samples indicating the disappearance of the chromophore and the formation of photoproducts. The rate of disappearance, evidence of the photochemical degradation rate, was estimated by plotting both the maximum absorbance wavelength and the absorbance values versus time of exposure. PABA maximum absorbance wavelength decreased more rapidly than that of

PABA-alginate complex. However, almost the same value of wavelength was reached by both products after 2 h sun exposure (Fig. n. 6).

No significant difference was found between the slopes of absorbance versus exposure time plot (Fig. n. 7).

These findings could indicate a similar disappearance of sunscreen by irradiation and then a similar photochemical degradation rate. Presumably, the amino group protection by electrostatic bindings do not prevent PABA photolysis reactions.

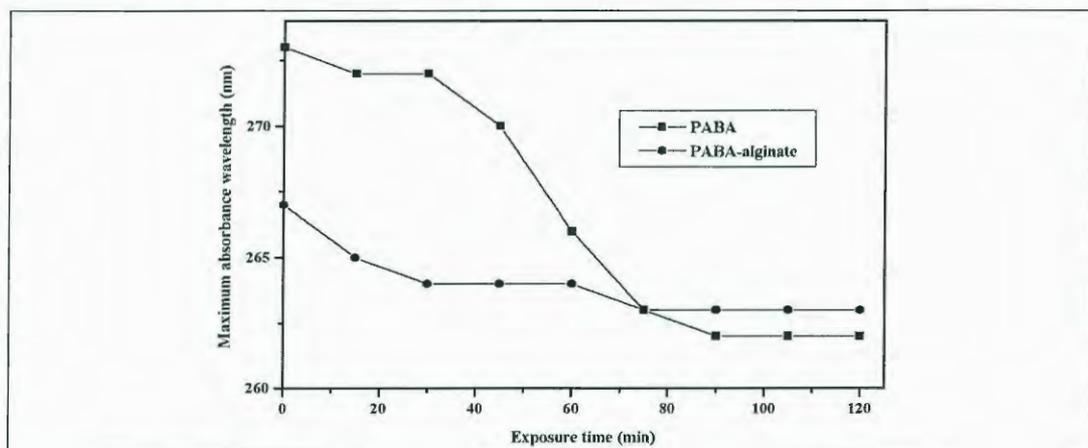


Fig. 6 Maximum absorbance wavelength shift of PABA and PABA-alginate solutions upon irradiation.

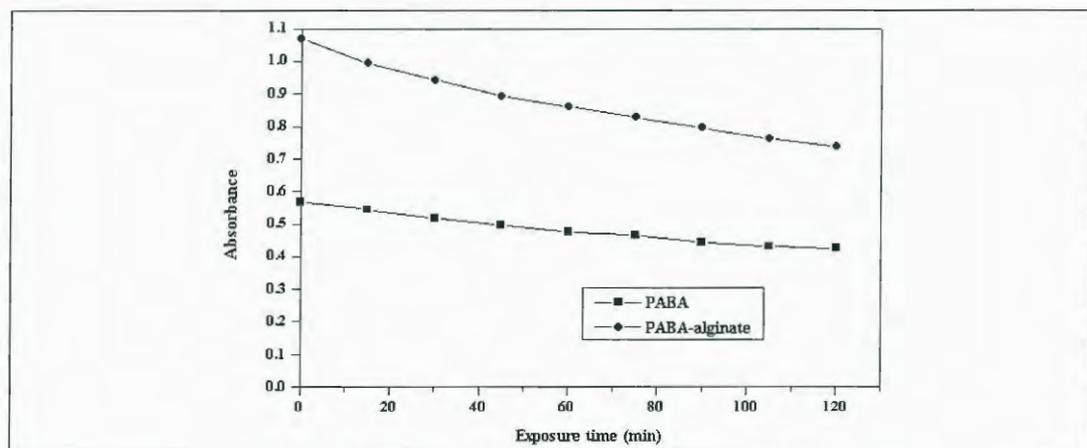


Fig. 7 Absorbance changes of PABA and PABA-alginate solutions upon irradiation.

CONCLUSIONS

PABA and PABA in a complex with alginate demonstrated a comparable photodegradation upon UV irradiation. Notwithstanding this, the complex showed a higher absorbance property and, consequently, higher photoprotection capacity than PABA. Therefore, lower screening amounts, inducing a less harmful photoproduct formation, would be requested to provide the same sun protection factor.

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