

Improvement of the mechanical properties of chitosan-alginate wound dressings containing silver through the addition of a biocompatible silicone rubber

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ABSTRACT: The benefits of associating chitosan with alginate for the production of wound dressings are well documented. However, the mechanical resistance of these devices is limited. This work aimed to improve the mechanical properties of chitosan-alginate membranes both with and without the microbicide agent AlphaSan[®] RC2000 (silver sodium hydrogen zirconium phosphate) by incorporating the liquid silicone rubber Silpuran[®] 2130 A/B. Membranes containing AlphaSan[®] RC2000 but without Silpuran[®] 2130 A/B have increased opacity, thickness, and water absorption, but low stability in water and tensile strength. The silicone gel remained in the structure of the formulations even after successive washing steps and its inclusion in the membranes reduced their thickness and swelling in aqueous media, improving their homogeneity, adhesiveness, stability, tensile strength, and flexibility. Thus, the addition of Silpuran[®] 2130 A/B proved to contribute positively to many relevant, particularly mechanical, properties of chitosan-alginate wound dressings whether or not they contained AlphaSan[®] RC2000. © 2014 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* **2015**, *132*, 41686.

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INTRODUCTION

The skin is the largest organ of the body and this living tissue has its own metabolism, which strongly contributes to overall body function. Thus, lesions to this organ may have consequences for the physical and mental health of a patient, since they can cause significant physiological imbalance and allow microbial contamination and proliferation.¹

Skin lesions, particularly open wounds, may be caused by surgery, trauma (due to mechanical, chemical, or physical agents) or ulceration.² Treatment of skin wounds is dynamic and the type of approach adopted depends on the kind of lesion and of the healing phase. There are various types of commercially available dressings for this purpose, but choice depends on factors intrinsic and extrinsic to the injury.

An ideal dressing should provide an optimal healing environment, protecting the wound, promoting skin recombination, maintaining a moist environment at the lesion interface, allowing gas exchange, acting as a barrier to microorganisms (thus preventing infection), and facilitating the removal of excess exudate in addition to being nontoxic and nonallergenic.³ The dressing should also have mechanical properties that facilitate

its application and removal and maintain its flexibility during the healing process.⁴

A single dressing type usually does not meet all the requirements for application on all classes of wounds. However, over the years technological advances have contributed to making available on the market products that can accelerate healing and significantly improve the quality of life of patients. However, commonly due to high costs, regrettably only a small fraction of all patients have access to some of the improved-healing dressing modalities.

Currently, efforts are also being focused on the use of materials of biological origin that may be able to accelerate the healing process at cellular and molecular levels,³ such as biopolymers capable of maintaining a suitably controlled microenvironment at the injury site. Different types of biopolymers with appropriate mechanical, physical, and biological properties are available in bulk amounts at relatively low cost; two such biopolymers are chitosan and alginate, biocompatible, and biodegradable materials that are already widely used in the production of dressings.⁵

Chitosan is a cationic character polymer derived from chitin, a component of the crustacean exoskeleton composed of *N*-acetyl

glucosamine and primarily of D-glucosamine units. It is known in the wound treatment field for its haemostatic properties and also for its stimulation of cell proliferation in addition to its bactericidal and fungicidal properties.^{6,7} Alginate is an anionic biopolymer obtained from brown algae and consists of 1-4- β -D-mannuronate (M) and α -L-guluronate (G) blocks. Its use in wound healing is related to its ability to provide a humid environment when in contact with the lesion, facilitating the re-epithelialization process. The sodium ions in the wound fluid slowly convert the calcium-crosslinked alginate in the dressing into a viscous solution of sodium alginate that relieves pain.^{8,9}

When mixed in aqueous phase at adequate pH levels, chitosan, and alginate combine spontaneously through strong electrostatic attraction to form a polyelectrolyte complex (PEC).^{10,11} The carboxyl groups in the alginate interact with the amino groups in the chitosan, resulting in a material with a high swelling tendency in physiological fluids and improved stability.¹² Furthermore, the ionic interaction enables varying the characteristics related to the materials' pH sensitivity, allowing also the immobilization of cells, enzymes, and therapeutic agent.¹³ The chitosan-alginate complex may be employed for the production of thin, transparent membranes, more efficient than conventional dressings regarding the controlled release of materials incorporated in them in comparison to the isolated polysaccharides.^{7,14} However, limitations such as low tensile strength and low flexibility may affect the integrity of the material during its storage, handling, and use on lesions. These limitations consist in one of the major drawbacks of the use of polysaccharide films as wound dressings.

This work aimed at evaluating the effects of adding the silicone liquid rubber Silpuran[®] 2130 A/B to formulations of chitosan and alginate membranes both with and without the silver-containing antimicrobial agent AlphaSan[®] RC2000 to improve the overall mechanical properties of the dressings. AlphaSan[®] RC2000 contains 10% of silver in its composition. Different proportions of this antimicrobial agent have already been tested in chitosan-alginate membranes and the results showed that formulations containing 1.1% of silver presented satisfactory antimicrobial efficacy against *Pseudomonas aeruginosa* and *Staphylococcus aureus*.¹⁵ Thus, the incorporation of antimicrobial compounds, such as silver, in chitosan-alginate membranes consist in a relevant strategy for application in dressings to be used in infected wounds aiming not only to control microbial growth but also to improve healing as a function of the polysaccharide components. Silpuran[®] 2130 A/B is a polydimethylsiloxane (PDMS) polymer comprising two components (A and B) with functional groups and auxiliaries for additional crosslinking mediated by a platinum catalyst. The mixture of components A and B forms a soft, tacky silicone adhesive, which after thermal vulcanization is highly transparent and chemically inert. Its composition does not include organic plasticizers, thus complying with medical standards. Since the siloxane chains of silicone compounds can adopt various configurations, its addition to chitosan and alginate complexes could also contribute to increase the flexibility of the polysaccharides. Given that platinum also binds easily to compounds having amino groups, the

addition of Silpuran[®] 2130 A/B could also contribute to the formation of more stable chitosan-containing complexes.¹⁶

EXPERIMENTAL

Materials

Chitosan-alginate membranes were produced using chitosan (Sigma-Aldrich, lot number 109K0043V with a degree of deacetylation of 96%), sodium alginate of low viscosity obtained from *Macrocystis pyrifera* (Sigma-Aldrich, lot number 090M0092V), AlphaSan[®] RC2000 (Milliken & Company), Silpuran[®] 2130 A/B (Wacker Chemie AG), glacial acetic acid, calcium chloride dihydrate, and sodium hydroxide (Merck). The water used throughout the work was distilled and deionized in a Milli-Q system (Millipore).

Production of the Membranes

Chitosan-alginate membranes were prepared by incorporation of 10% (w/w) Silpuran[®] 2130 A/B in relation to the polysaccharides both with and without 11% AlphaSan[®] RC2000. The method was based on procedures proposed by Rodrigues *et al.*¹⁷ and Bueno and Moraes¹⁸ and adapted by Girata.¹⁵ First, with a peristaltic pump (Model Minipuls 3, Gilson), 90 mL of 1% (w/v) chitosan in 2% (v/v) aqueous acid solution were added at a rate of 200 mL/h to 180 mL of an aqueous solution of alginate at 0.5% (w/v) in a jacketed stainless steel reactor with an internal diameter of 10 cm and a height of 20 cm. During the mixing step, the system temperature was kept at 25°C using a water bath (model 214 M2, Quimis). A mechanical stirrer (251 D, Quimis) having inclined blades with a radius of 2.1 cm was used for stirring at 500 rpm. At the end of this step, the rate was increased to 1000 rpm and the mixture was stirred for another 10 min. Then 13.0 mL of NaOH aqueous solution at 2 mol/L was added to the suspension to elevate the pH to 7.0 and the same stirring rate was maintained for 10 additional minutes. When required, 90 μ L of Silpuran[®] 2130 A and 90 μ L of Silpuran[®] 2130 B were added to the mixture separately with a 5 min interval in between additions. The stirring rate and temperature were kept constant for another 10 min. Then 3.6 mL of 2% (w/v) CaCl₂ aqueous solution were added to crosslink carboxyl groups of the alginate which were not complexed with chitosan amino groups. After 10 min, 0.2 g of AlphaSan[®] RC2000 was added to the formulations under stirring for 5 min at a rate of 500 rpm. The polymer mixtures obtained were deaerated for 120 min with the aid of a vacuum pump (Q-355B2, Quimis). The mixture was then transferred to two polystyrene Petri dishes (15 cm in diameter) and dried in an oven with air circulation (410D, Nova Ética) at 60°C for 6 h. After drying, the samples were immersed in 150 mL of 2% (w/v) CaCl₂ aqueous solution for 30 min for the reticulation of the remaining free carboxyl groups from the alginate. The films were then washed twice for 30 min with 200 mL of deionized water. The final drying step was performed at room temperature for 24 h. The samples were then sterilized with ethylene oxide (EO) by exposure to Oxyfume-30 (30% EO and 70% carbon dioxide) at 40°C for 8 h at a relative humidity of 30–80%. The residual EO was removed by aeration of the samples during 48 h. All membranes containing silver were prepared and stored in indirect light to avoid darkening.

Determination of Membrane Characteristics

The samples were characterized with respect to morphology, Fourier transform infrared spectroscopy (FTIR), energy dispersive X-ray spectroscopy (EDS), thickness, degree of swelling and stability in aqueous solutions and mechanical strength, as described below.

Morphology

The morphology of the surface and of the cross-section of the membranes was examined using a scanning electron microscope (LEO 440i model, Leica). Samples ($2 \times 1 \text{ cm}^2$) were lyophilized, transferred to suitable supports, and metalized (mini Sputter coater, SC 7620) by depositing a thin layer of gold (92 Å).

Energy Dispersive X-ray Spectroscopy (EDS) Analysis

EDS analysis was performed to detect the presence of silver and silicon in the samples used to carry out the scanning electron microscopy study.

Fourier Transform Infrared Spectroscopy Analysis

Analysis of the Fourier transform infrared spectroscopy spectra using the attenuated total reflectance spectroscopy method (FTIR-ATR) was performed for wave numbers ranging from 4000 to 675 cm^{-1} in a Nicolet 6700 spectrophotometer (ThermoScientific). The samples ($2 \times 1 \text{ cm}^2$) were kept in a desiccator for 24 h prior to analysis. A total of 64 scans was acquired at a 4 cm^{-1} resolution.

Thickness

Membrane thickness was measured using a micrometer (Digimess). Nine measurements were taken at different positions along the length of each membrane and the mean value was calculated.

Swelling and Stability in Aqueous Solutions

The gradual degree of swelling of the dried membranes in water, 0.9% (w/v) NaCl aqueous solution (SS), simulated body fluid (SBF) prepared according to Kokubo *et al.*¹⁹ and fetal bovine serum (FBS) was analyzed. Dry samples ($6 \times 1 \text{ cm}^2$) with known mass (M_i) were immersed in 10 mL of each solution at 37°C for 24 h. After this period, the samples were weighed again to determine the final mass (M_f). The degree of swelling (S) of each solution was calculated using Eq. (1):

$$S = \frac{M_f - M_i}{M_i} \times 100 \quad (1)$$

Next the wet samples were dried in an incubator at 37°C until reaching constant weight (M_c). Then the samples were stored in a desiccator for 24 h, and at the end of this period, membrane stability was evaluated in terms of mass loss (L) using Eq. (2).

$$L = \frac{M_i - M_c}{M_i} \times 100 \quad (2)$$

All measurements were performed in triplicate.

Mechanical Properties

The mechanical properties of the membranes (ten $8 \times 1 \text{ cm}^2$ samples for each formulation) were evaluated using a texturometer (model TA.XT2, Stable Microsystems SMD), based on adaptations of ASTM D-882-95a.²⁰ The initial grip separation was of 5 cm and the crosshead speed was 0.1 cm/s. The tensile

strength and elongation at break were calculated according to Eqs. ((3) and (4)), respectively.

$$T = \frac{F_m}{A_s} \quad (3)$$

$$E = \frac{dr - d_i}{d_i} \times 100 \quad (4)$$

where F_m is the maximum strength, A_s is the cross-sectional area of the sample, d_i is the initial distance between the texturometer grips (5 cm) and dr is the distance between the grips at the time of sample break.

RESULTS AND DISCUSSION

Aspect and Morphology of Membranes

The alginate-chitosan membranes prepared with the antimicrobial agent AlphaSan[®] RC2000 were whitish, unlike the membranes prepared without it, which were translucent as shown in Figure 1.

The addition of the silicone gel Silpuran[®] 2130 A/B also reduced the transparency of the membranes. Given that the silicone gel was poorly miscible with the chitosan-alginate mixture, it was dispersed in the matrix in the form of small droplets, resulting in a flexible matrix with the appearance of a foam sheet, as illustrated in Figure 2. The concentration of 10% of the silicone agent with respect to total weight of polysaccharide was chosen considering, in addition to adequate final homogeneity of the product, increased flexibility of the membranes with easy handling of the materials involved during processing.

According to Colas and Curtis,¹⁶ silicone elastomers can be easily transformed into a stable three-dimensional network due to their ease of crosslinking, even at mild temperatures. Silpuran[®] 2130 A/B vulcanizes rapidly at 100°C , but in the case of the biomaterials developed, vulcanization of this compound in the mixture probably occurred during the chitosan-alginate PEC six-hour drying step at 60°C .

The results of the surface morphology analysis performed by scanning electron microscopy are shown in Figure 3. Silicone polymer droplets or bubbles can be clearly observed both at the surface and between the lamellae in the samples with Silpuran[®] 2130 A/B.

Because of the high viscosity of the PEC suspension, air bubbles may have been trapped in the structure of the matrix, contributing to dispersion of the silicone gel in the form of round aggregates. According to Fawcett *et al.*,²¹ films containing silicone elastomers may also have bubbles generated during the deaeration process or due to reactions that generate gas from silicone constituents, such as the hydrogen resulting from the Si-H polymers reacting in the presence of platinum-based catalysts, as is the case with Silpuran[®] 2130 A/B.

The antimicrobial agent incorporated into the formulations seemed to be relatively evenly distributed in the membrane matrix, forming small agglomerates that could be observed throughout the samples.

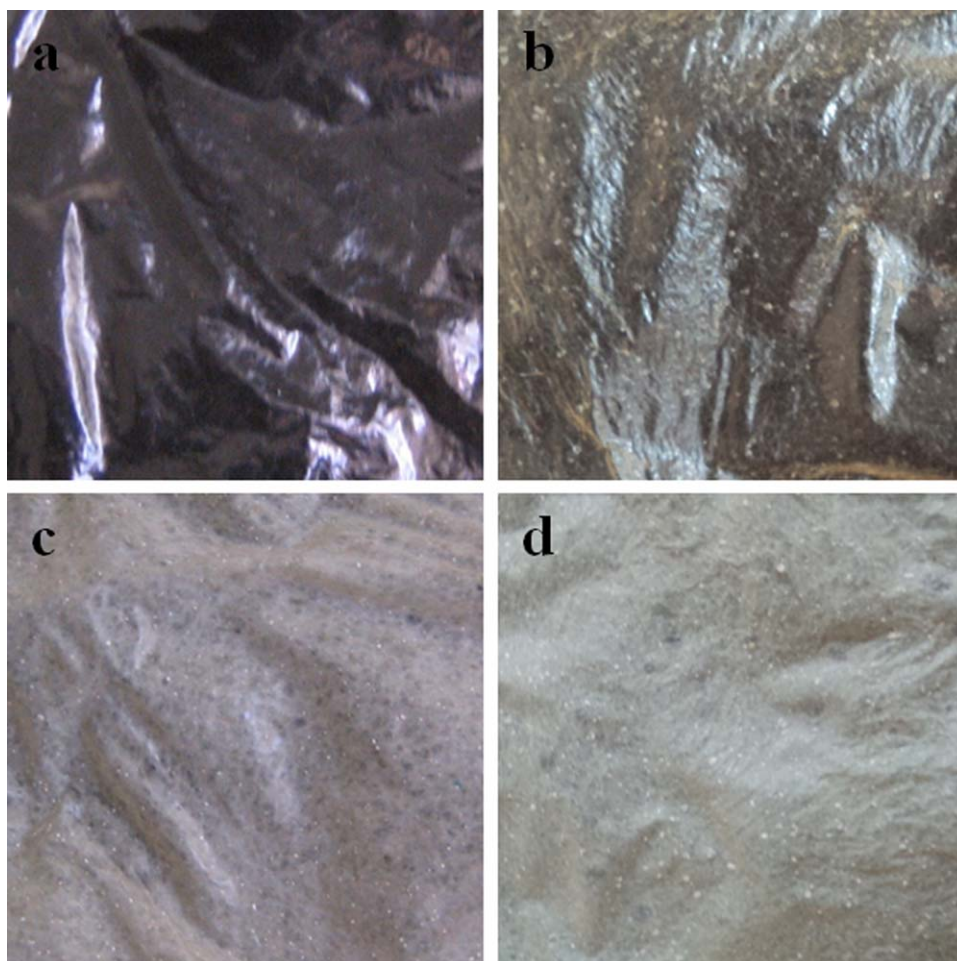


Figure 1. Visual aspects of the alginate-chitosan membranes: Formulations without AlphaSan[®] RC2000 and without (a) and with (b) Silpuran[®] 2130 A/B and formulations with AlphaSan[®] RC2000 and without (c) and with (d) Silpuran[®] 2130 A/B. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Surface Composition Analysis

EDS and FTIR analyses were performed to verify the presence, form of distribution and interaction of the different components of the membranes. Typical aspects of the spectra obtained for the formulations containing Silpuran[®] 2130 A/B and the sil-

icon and silver mapping by EDS are shown in Figures 4 and 5, respectively.

Silicon was detected in the samples containing Silpuran[®] 2130 A/B, indicating that the PDMS polymer had not been removed from the formulations during the washing step. Calcium and

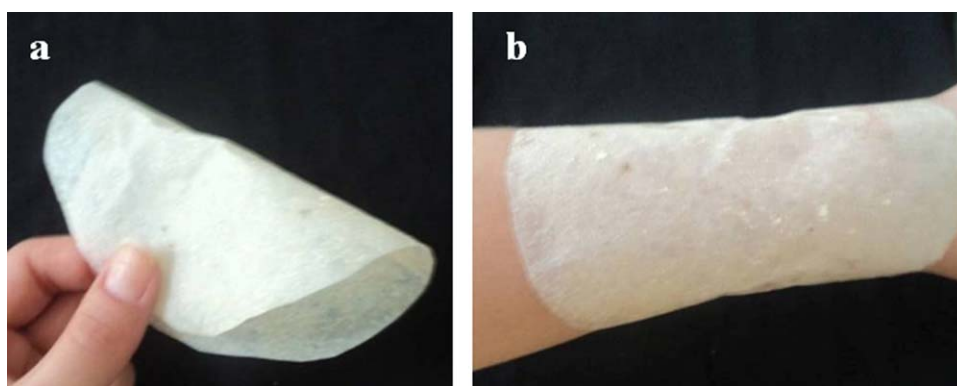


Figure 2. Flexibility (a) and adhesiveness (b) of formulations prepared with 10% Silpuran[®] 2130 A/B and 11% AlphaSan[®] RC2000. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

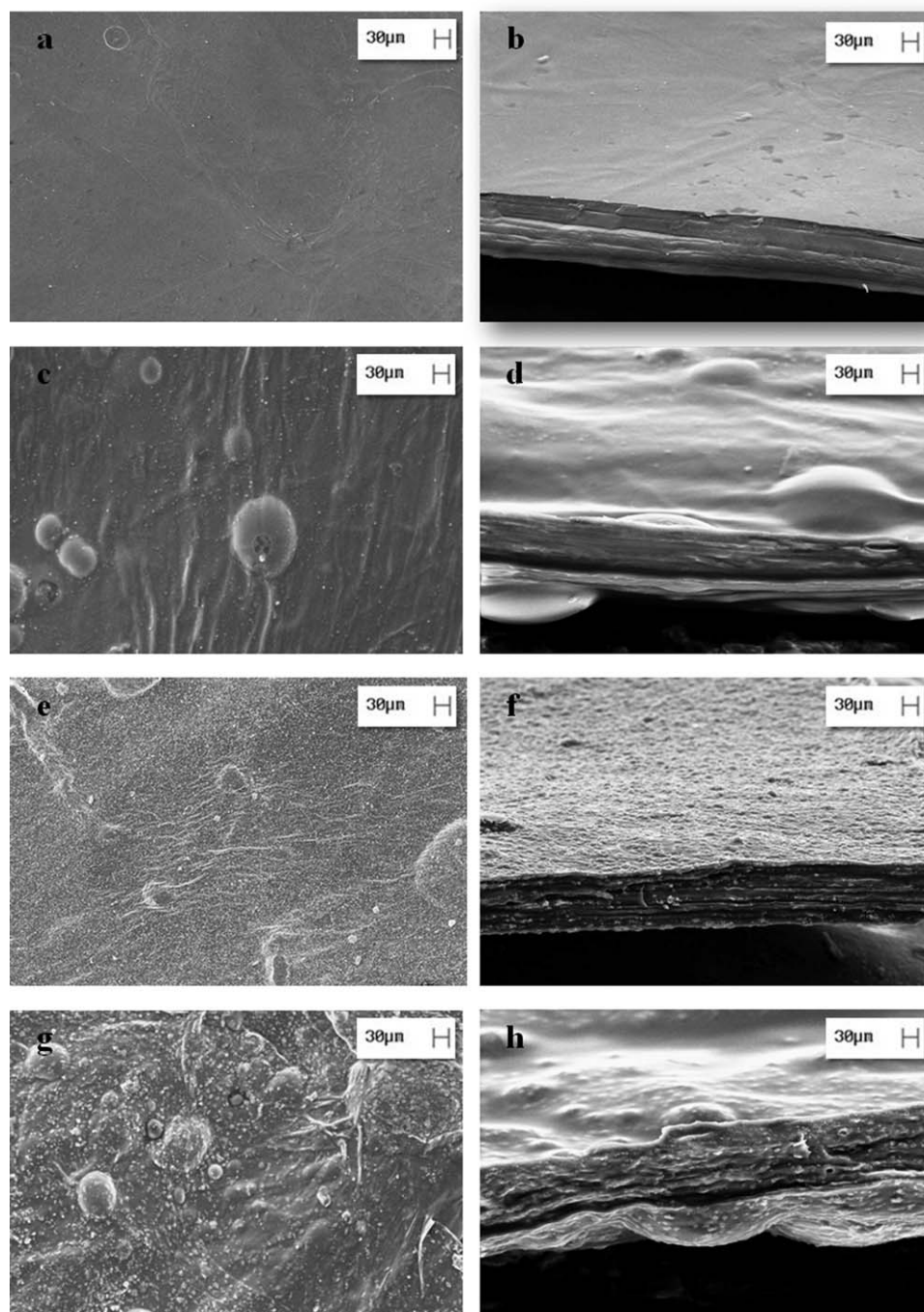


Figure 3. Surface morphology and cross-sections of formulations without AlphaSan[®] RC2000 and without (a, b) and with (c, d) Silpuran[®] 2130 A/B and formulations with AlphaSan[®] RC2000 and without (e, f) and with (g, h) Silpuran[®] 2130 A/B.

chlorine were also detected in both formulations, which can be explained by the addition of $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$ during the ion-reticulating steps. The peaks of gold in Figure 4(a,b) are related to the sample metallization procedure required to perform the SEM analysis. As expected, silver and phosphorus were detected only in the samples containing AlphaSan[®] RC2000, which consists of silver sodium hydrogen zirconium phosphate. The proportion of silver detected was low [Figure 4(b)], and its detection by EDS coupled with the SEM membrane analysis in

Figure 5(b,c) showed only homogeneously distributed faint purple dots. However, these observations had been expected, since only 1.1% in weight of silver was added to the formulation in comparison to the total amount of polysaccharides in the devices.

Regions rich in silicon can be noted in Figure 5. As discussed above, these aggregates may have resulted from the migration of the silicone polymer to the less hydrophilic vicinity of the

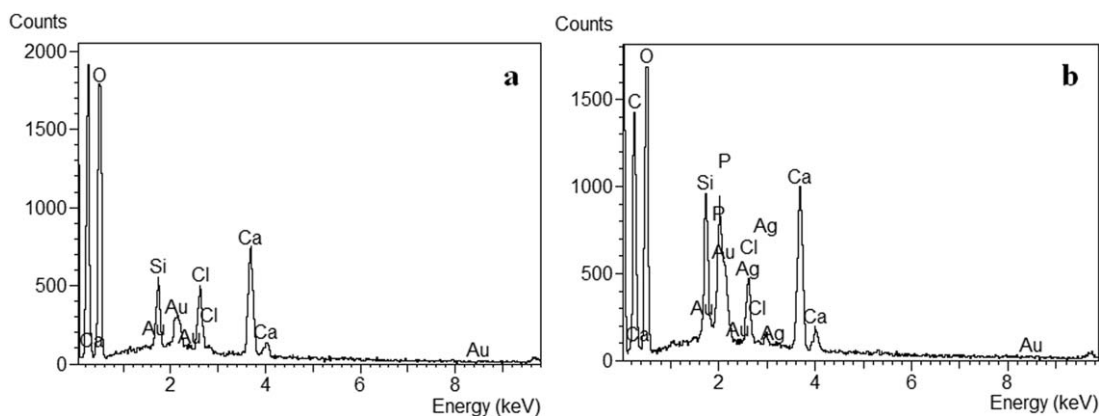


Figure 4. Typical EDS spectra of formulations containing 10% Silpuran[®] 2130 A/B: membrane without (a) and with (b) AlphaSan[®] RC2000.

bubbles formed during the mixing process, during either deaeration or the silicone gel crosslinking step.

The FTIR-ATR absorption spectra of the samples both with and without Silpuran[®] 2130 A/B and with and without AlphaSan[®] RC2000 are shown in Figure 6. The characteristic absorption peaks, which can be used to identify the compounds in the membranes, are shown in Table I. As can be observed in Figure 6(a,b), all absorption spectra show a broad band around the 3600–3000 cm^{-1} region. According to Lawrie *et al.*,²² this band

can be attributed to the stretching of the —OH groups in both alginate and chitosan.

The peaks related to the chitosan amino groups and the alginate carboxylate (around 1580 and 1600 cm^{-1} , respectively) overlap.^{22,23} Thus, with the FTIR analysis, it is difficult to identify the presence of either free compound or its protonation state or of any interaction between them.

As noted by Sheng *et al.*,²⁴ the peak at 1612 cm^{-1} refers to the COO—M binding, where M may be Na^+ , K^+ , Ca^{++} , or Mg^{++} .

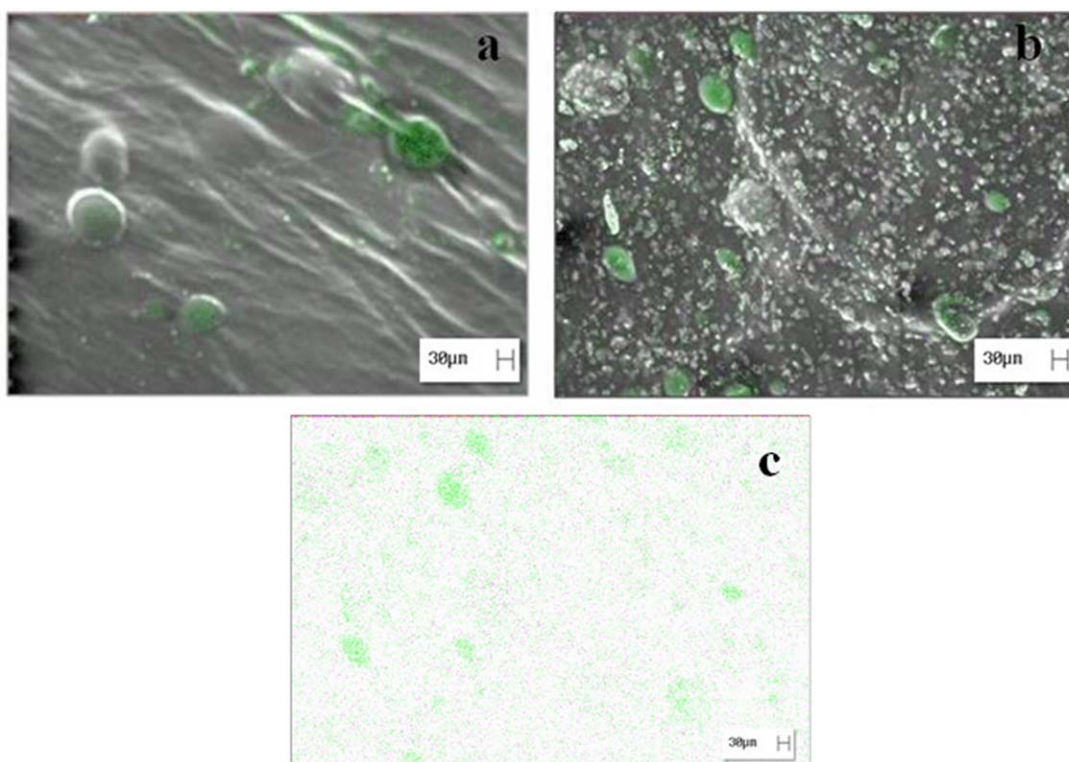


Figure 5. Mapping of silicon (in green) and silver (in purple) in formulations prepared with 10% Silpuran[®] 2130 A/B and without (a) and with (b) AlphaSan[®] RC2000. In the image shown in (c), the aspect of the membrane was deleted from the background to improve the contrast and facilitate observation of silicon deposits and homogeneously dispersed silver. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

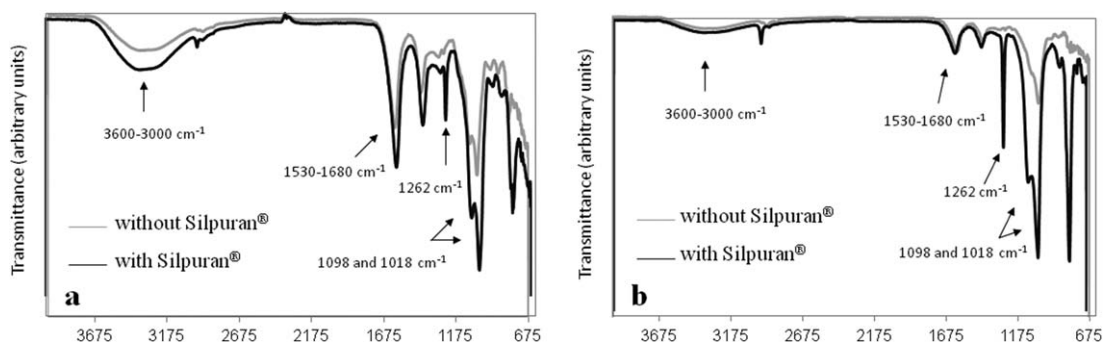


Figure 6. Absorption spectra (FTIR-ATR) of the chitosan-alginate samples without (a) and with (b) AlphaSan® RC2000.

Since AlphaSan® RC2000 contains Na^+ , and in view of the overlapping of this peak with the chitosan-alginate PEC band, it is possible that the sodium ions of the antimicrobial agent interacted with the carboxyl groups of the alginate, as well as the Na^+ ions originated from the sodium alginate used. Furthermore, the Ca^{++} ions of the crosslinking solution (CaCl_2) may also have interacted with free carboxyl residues from the alginate. This peak is not shown clearly in Figure 6(a,b) because it is within the range of 1530 to 1680 cm^{-1} .

According to the National Industrial Chemicals Notification and Assessment Scheme,²⁵ the antimicrobial agent AlphaSan® RC2000 has an absorption peak at 1039 cm^{-1} related to the PO binding. However, this peak is not clearly visible in the analysis of the samples, probably due to the overlapping of the bands with peaks between 1098 and 1018 cm^{-1} . Nevertheless, the presence of the antimicrobial agent is easily detected by the naked eye and confirmed by the SEM and EDS analyses, as previously discussed.

The occurrence of pronounced peaks at around 1260, 1019, and 800 cm^{-1} can be noted. Liu *et al.*,²⁶ observed that PDMS has an acute peak at 1262 cm^{-1} that is characteristic of the $\text{Si}-\text{CH}_3$ bond as well as the large double peaks characteristic of $\text{Si}-\text{O}-\text{Si}$ bonds at 1098 and 1018 cm^{-1} .

Therefore, using this method it can be confirmed that both AlphaSan® RC2000 and Silpuran® 2130 A/B can be incorpo-

Table I. Chitosan, Alginate, PDMS, and AlphaSan® RC2000 Characteristic FTIR Absorption Peaks

Peak (cm^{-1})	Group	Compound	References
799	$-\text{Si}-\text{CH}_3$	PDMS	20
1018	$-\text{Si}-\text{O}-\text{Si}$	PDMS	20
1039	$-\text{P}-\text{O}$	AlphaSan®	21
1262	$-\text{Si}-\text{CH}_3$	PDMS	20
1405	$-\text{COOH}$	Alginate	22
1560	$-\text{NH}$	Chitosan	22
1580	$-\text{NH}_2$	Chitosan	22
1600	$-\text{COOH}$	Alginate	22,23
1650	$-\text{C}=\text{O}$ of the amide group	Chitosan	23

rated into chitosan-alginate dressings successfully, since none of the aforementioned compounds seem to have been substantially removed from the devices during the washing step.

Thickness, Swelling and Stability of Samples

The mean values for thickness; swelling in water, 0.9% NaCl aqueous solution (SS), simulated body fluid (SBF), and fetal bovine serum (FBS) at 37°C for 24 h; and mass loss of the membranes when exposed to the same solvents are shown in Table II.

The incorporation of Silpuran® 2130 A/B in the formulation without AlphaSan® RC2000 resulted in a 78% decrease in the thickness of the samples, while with AlphaSan® RC2000, the decrease was of 81%. An increase in the thickness of the membranes without the silicone gel, but with the antimicrobial agent, was also observed. Given that the solubility of AlphaSan® RC2000 in aqueous solutions is very low (maximum solubility in water is 2.6×10^{-4} g/L at 20°C according to the National Industrial Chemicals Notification and Assessment Scheme²⁵), this compound was dispersed throughout the membranes in the form of solid aggregates, which could be observed by SEM, as already pointed out, thereby significantly increasing the thickness of the membranes.

A reduction in thickness after addition of a silicone-based polymer to nonwoven polyester dressings was also observed by Losi *et al.*²⁷ These authors mention that the silicone coating of the original material reduced the overall thickness of the dressing from 15 to 12 mm, also resulting in a smoother and more homogenous appearance. The reduction in dressing thickness is of particular interest, since it can provide extra benefits such as increased comfort to the patient.

According to Ma *et al.*,²⁸ artificial skin substitutes should generally be thinner than the human dermis, whose thickness ranges from 0.5 to 2 mm depending on age, sex, and body area. Thus, all membranes prepared in this work have the potential for successful use as skin dressings.

The addition of Silpuran® 2130 A/B to the membranes without AlphaSan® RC2000 tended to slightly decrease absorption of all solutions, while its addition to membranes with AlphaSan® RC2000 had a more pronounced tendency to increase absorption of the solutions (except for samples in water). This may be

Table II. Values for Thickness, Swelling, and Mass Loss of the formulations Prepared with and Without AlphaSan[®] RC2000 and with and Without Silpuran[®] 2130 A/B

Property		Formulation			
		Without AlphaSan [®]		With AlphaSan [®]	
		Without Silpuran [®]	With Silpuran [®]	Without Silpuran [®]	With Silpuran [®]
Thickness (μm)		56.67 ± 4.08 ^a	11.66 ± 0.21 ^b	94.40 ± 3.90 ^c	16.83 ± 0.40 ^d
Swelling (g/g)	Water	4.19 ± 0.24 ^e	3.09 ± 0.19 ^{e,f}	6.48 ± 1.07 ^{e, g}	5.46 ± 90 ^e
	SS	11.91 ± 0.4 ^{h,i}	8.06 ± 0.43 ^{h, j}	8.33 ± 0.86 ^{h,j}	13.91 ± 1.64 ⁱ
	SBF	9.85 ± 0.42 ^k	6.32 ± 0.38 ^l	5.73 ± 0.20 ^l	8.59 ± 0.41 ^k
	FBS	9.66 ± 0.33 ^m	6.52 ± 0.35 ^{m,n}	7.77 ± 0.44 ^{n,o}	8.53 ± 0.47 ^{m,n}
Mass loss (%)	Water	10.75 ± 0.19 ^p	2.34 ± 0.32 ^q	15.34 ± 5.92 ^p	1.92 ± 0.37 ^q
	SS	15.34 ± 1.03 ^r	8.20 ± 0.54 ^s	11.53 ± 0.95 ^s	4.14 ± 0.49 ^t
	SBF	13.28 ± 0.95 ^u	5.98 ± 0.70 ^v	12.40 ± 0.72 ^u	1.17 ± 0.21 ^x
	FBS	13.99 ± 11.7 ^y	4.48 ± 0.77 ^w	6.37 ± 3.58 ^z	3.55 ± 0.30 ^w

The same superscript letter on the same line indicates that there is no significant difference between the mean values (Tukey test, $p < 0.05$).

due to interference by the ionic force of these solutions. According to Maurstad *et al.*²⁹ and Bartkowiak,³⁰ the presence of ions can shield the charge of polysaccharides in solution by forming a counter-ion cloud that reduces electrostatic repulsion between the chains. In addition, according to Bueno and Moraes,¹⁸ the higher the medium's ionic concentration, the greater is the proximity between the chains of polysaccharides, creating a more closely packed and stable structure which impairs permeability of the PEC matrix by the solutions.

Addition of the silicone compound resulted in a significant increase in the stability of the membranes when in contact with all the aqueous media, with a maximum mass loss of 8% in SS. This result may be attributed to the fact that Silpuran[®] 2130 A/B has a hydrophobic nature, probably making full hydration of the polysaccharide molecules to the point of solubilization and removal from the matrix structure more difficult. Also, given that membranes containing Silpuran[®] 2130 A/B are thinner, it is reasonable to suppose that their structure is more reticulated, and consequently, less prone to expand, making the solubility, mobility and release of free polysaccharide chains more difficult. Thus, it can be observed that the stability of formulations con-

taining silicone, both with and without AlphaSan[®] RC2000, is relatively high, enabling their use as dressings on wet lesions for at least one week before dressing change is required.

Mechanical Properties of the Membranes

A dressing should have mechanical properties that are adequate for application, easy handling and storage. The results on tensile strength and percent elongation of the chitosan-alginate membranes with and without AlphaSan[®] RC2000 and Silpuran[®] 2130 A/B are shown in Table III.

The devices prepared with the antimicrobial agent showed a decrease in tensile strength. This can be attributed to the tendency of the chitosan-alginate PEC structure to break at regions where there are high levels of antimicrobial agent agglomeration.

However, a significant increase in the flexibility and tensile strength of formulations containing the silicone compound, both with and without AlphaSan[®] RC2000, was observed. This may be credited to many factors. First, the silicone compound was fairly evenly distributed throughout the structure of the matrix and the crosslinking of the Silpuran[®] 2130 A/B polymer chains at different points in the chitosan-alginate PEC favored the formation of a matrix with a more resistant structure. Second, according to Colas and Curtis,¹⁶ platinum binds easily to compounds having amino groups (such as those in chitosan), which could also have contributed to the formation of a more mechanically stable matrix. Finally, the siloxane chains in Silpuran[®] 2130 A/B can adopt various configurations, having the potential to decrease the rigidity of the structure, and consequently, to significantly improve the overall flexibility of the material.

Despite the significant increase in tensile strength, the elongation at break of the membranes containing silicone gel practically did not improve. Low percent elongations of between 3 and 5% were observed for all formulations. Considering that normal skin may stretch around 70–75%,³¹ the use of these materials in body areas with high mechanical requirements, such as knees and elbows, is not recommended.

Table III. Mechanical Properties of Membranes Prepared with and Without Adding AlphaSan[®] RC2000 and Silpuran[®] 2130 A/B

Formulation	Tensile strength (MPa)	Elongation at break (%)
Without AlphaSan [®] and Silpuran [®]	20.45 ± 1.38 ^a	2.78 ± 0.3 ^a
With only AlphaSan [®]	4.90 ± 0.83 ^b	3.66 ± 0.2 ^a
With only Silpuran [®]	63.13 ± 5.52 ^c	5.14 ± 0.2 ^a
With AlphaSan [®] and Silpuran [®]	43.50 ± 5.56 ^d	3.88 ± 0.5 ^a

The same superscript letter in the same column indicates that there is no significant difference between the mean values (Tukey test, $p < 0.05$).

CONCLUSIONS

The effect of incorporating the silicone agent Silpuran[®] 2130 A/B into chitosan-alginate membranes both with and without the antimicrobial agent AlphaSan[®] RC2000 was evaluated, aiming to improve the mechanical properties of these devices. Membranes containing the silicone rubber had a more homogeneous appearance and adequate flexibility and adhesiveness. Moreover, there was a decrease in thickness of these formulations, both with and without incorporation of AlphaSan[®] RC2000. The addition of Silpuran[®] 2130 A/B to the membranes without the antimicrobial agent resulted in a decrease in absorption of all solutions, while addition to formulations containing AlphaSan[®] RC2000 resulted in an increase in SS and SBF absorption. All membranes containing silicone showed appreciably greater stability when in contact with different physiological solutions. A significant increase in tensile strength in formulations containing the silicone compound, both with and without the antimicrobial agent, was observed (43.50 and 63.13 MPa, respectively). However, the elongation at break of these devices did not improve. Chemical analysis by EDS and FTIR confirmed that the silicone agent had not been removed during the membrane-washing step. Thus, incorporation of Silpuran[®] 2130 A/B proved to be a good alternative for improving the mechanical properties of chitosan-alginate dressings, since this approach did not result in the loss of other properties deemed important for the desired application.

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