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PRODUCTION OF ALGINATE, CHITOSAN AND ALGINATE/CHITOSAN FIBERS AND EVALUATION OF PHYSICOCHEMICAL, MORPHOLOGICAL AND CYTOTOXIC PROPERTIES

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ABSTRACT

In this study fibers from alginate, chitosan and hybrid alginate/chitosan with and without glycerol were synthesized. The fibers were characterized by Scanning Electron Microscopy (SEM), Differential Scanning Calorimetry (DSC), and Thermogravimetry (TGA). Properties such as tensile, swelling, weight loss and cytotoxicity were evaluated. The water absorption considering a period of 30 days for alginate fibers without glycerol were 161% , 167% for alginate with glycerol, 100% for chitosan, chitosan with glycerol 158% and 215% e 156% for the hybrid fibers without and with glycerol respectively. The weight loss was 26% for alginate without glycerol, 28% for alginate with glycerol, 15% for chitosan without glycerol, 28% for chitosan with glycerol, 23% for hybrid without glycerol and 27% for hybrid with glycerol fibers. All fibers had an average diameter between 75 and 100 µm. The glycerol increased the fiber elongation 24% for alginate fibers, 93% for chitosan fibers and 13% for hybrid fibers. All fibers without and with glycerol showed no cytotoxicity. The produced fibers satisfied the analysis criteria and presented potential for technical textile production for biomedical applications.

Keywords: Alginate. Chitosan. Fiber.

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INTRODUCTION

In the last decades textile industry is outstanding in its diverse production sectors, mainly in technical textiles, incorporating in processes all the new technologies developed in physical, chemical, and biological sciences [1,2].

The technical textiles or intelligent fabrics are structures specifically projected and developed for employment in products, processes, or services of almost all industrial areas [3]. The polymer, fibers, fabric technology, manufacture and equipment processes are factors that provided the major impact in technical textiles technology and market development. They combined different characteristics in the same product, as flexibility or stiffness, low weight, and strength [4].

These materials can be used in diverse industrial sectors as sportive articles, transports, civil construction, geotextiles, protection military articles and clothes and in medical area [2–4].

In the medical area, textile materials are increasingly important in many applications of fibers, fabrics, nonwoven in medical protection clothes confection, implantation, non-implantation, and extra-corporal devices [5].

The medical garment should protect the professionals from possibly contaminated fluids, bacteria, fungi, and viruses. However, besides the protection, the clothes should provide comfort and not limit the movements of the patients and professionals [6]. Considering implantations, the textile structures are identified by their construction, composition, fibers superficial behavior and degradation. In these cases, the main concern is the human body's reaction to the implantation. The textile materials employed in implantations must satisfy both mechanical requirements and biocompatibility. [7].

The purpose of a curative bandage is to protect the wound from further damage as well as to relieve the pain, absorb exudates and curb the bleeding [7].

An ideal dressing, to accelerate healing, should keep the wound at an ideal temperature, pH level, and moist (free of infection and excessive slough), maintaining a high humidity at the wound dressing interface, allowing gaseous exchange, free of toxic chemicals, particles or fibers that could be released from it and undisturbed to its structure changes[8]. It also should be hypoallergenic, non-toxic, and easily removed. In this way, the employment of biomaterials with antimicrobial and wound-healing properties is interesting [5,6].

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In recent years the interest in natural polymers, such as casein, collagen, soy, gluten, alginate, chitosan, and from other marine organisms, has increased considerably Textiles produced by biopolymers have good biocompatibility and low toxicity, suitable for application in biomaterials [9,10].

Between the biopolymers, alginate is a polysaccharide with a linear structure composed of unit glycoside links from β-D-mannuronic and α-L-guluronic acids, which can vary in their composition and sequence. The molar mass determines the agarose physicochemical properties, and it depends on the seaweed source from which the alginate was extracted [8].

Several pharmaceutical products are present in alginate [11]. Recent reports attest to its great potential to produce homopolymeric structures, as well as in tissue engineering employed as a hydrogel [11,12]. Alginate in combination with other polymers, such as collagen, has also been highlighted in biotechnology and biomedical research, as alginate is biocompatible, has a relatively low cost, is non-toxic, and its ability to form gels by adding divalent cations such as Ca^{2+}. The sodium and calcium salts of alginic acid were non-toxic and caused no histological changes The sodium and calcium salts of alginic acid were non-toxic and caused no histological changes (Ahmad Raus et al., 2021; Puscaselu et al., 2020).

The solubility of alginate depends on some parameters, such as solvent pH (it should be above a critical value), presence of gelling ions in the solvent, and medium ionic strength (changing it, solutions properties such as viscosity could be affected) [14].

Alginate can be employed in the pharmaceutical, nourishing, and textile industries [11,14,15]. In the medical area, the alginate dressing absorbs the exudate and protects the wounds. The material reacts with the exudate, forms a hydrophilic gel over the wound surface, and creates a moist environment [16] .

Chitosan is another important and abundant renewable biopolymer. It is obtained from a chitin deacetylation reaction, which is extracted from the exoskeleton of crustaceans [17]. Some chitosan properties as biodegradability, biocompatibility, low toxicity, versatility to form films, gels, fibers, beads, and scaffolds, and antimicrobial activity, are interesting for medical applications [18].

In the present study fibers from alginate and hybrid of alginate/chitosan with and without glycerol were synthesized. The aim was to obtain fibers with the potential to be used as raw material for technical textile production, mainly in the medical area.

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MATERIAL AND METHODS

REAGENTS

Sodium alginate (20.000-40.000 cps viscosity), crab extracted chitosan (85% deacetylation minimum) and all employed reagents were acquired from Sigma Co. (St. Louis, ME, USA).

Fiber Production

Alginate, chitosan and hybrid fibers with and without glycerol were produced by wet spinning technique with a syringe (Hypodermic syringes, polypropylene Luer-lock tip, capacity 10 mL, graduated, 25 x 7 mm and needle Ø 0.6 x L 2.5 mm).

Alginate 5% (m/v) was dissolved in 10 mL of ethanol and 90 mL of distilled water by stirring at room temperature overnight. Glycerol at 2.5% (m/m) was added to the solution. The sodium alginate solution with and without glycerol was injected into coagulation bath at 30ºC containing calcium chloride 2% (m/v). The resultant fibers were picked up from this coagulation medium after 24 h and washed three times with distilled water. The alginate filaments were rolled manually on the cylindrical polypropylene support. The fibers were dried at room temperature conditions during 24 h [19].

Chitosan 2.2 % (m/v) was dissolved in 200 mL of 2 % acetic acid (v/v) by stirring at room temperature overnight and subsequently adding 250 mL of methanol (v/v). The chitosan gel was filtered using a vacuum pump. The chitosan gel with and without glycerol was injected into a coagulation bath at 30 ºC containing 300 mL of 0.5 M sodium sulfate, 100 mL of 1 M sodium hydroxide and 600 mL of distilled water. The resultant fibers were extracted from this coagulation medium after 24 hours and placed in 50 % methanol for 2 h. Glycerol at 2.5% (w/w) was added into solution.

Hybrid fibers were produced extruding the alginate gel, with and without glycerol, in a solution containing 66% (v/v) calcium chloride solution and 33% (v/v) of 0.2% (m/v) chitosan gel. The fibers remained in the resultant solution for 24 h. After this, the fibers remained in 50% (v/v) methanol for 4 h. Finally, the alginate filaments were washed and rolled manually on the cylindrical polypropylene support to dry at room temperature.

WATER ABSORPTION AND WEIGHT LOSS ASSAYS

Water absorption (or swelling) and fiber weight loss were performed in triplicate. The fibers were weighed and immersed in 12 mL of deionized water. The flasks samples (15 mL)

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were closed with Parafilm film (Pechiney Plastic Packaging Co., Chicago, IL, USA) and placed into a thermo-regulated bath (TEC-420, Tecnal, Piracicaba, Brazil) under agitation (60 rpm), at 37ºC for 1, 3, 7, 15, 21 and 30 days. For water absorption an analytical balance (AUW220D, Shimadzu, São Paulo, Brazil) was employed to determine the initial fiber mass (mi) and, after incubation, being the excess solution removed with a filtering paper, the final mass (mw). Afterwards, fibers were dried at 40ºC until reaching constant weight to determine (mf). Water absorption and weight loss are given by equations 1 and 2.

$$\text{Water absorption} = \left[\frac{(mw-mi)}{mi}\right].100 \qquad \text{(Equation 1)}$$

$$\text{Weight loss} = \left[\frac{(mf-mi)}{mi}\right].100 \qquad \text{(Equation 2)}$$

MICROSTRUCTURAL ANALYSIS OF THE FIBERS

Microstructural analysis of the fibers was performed employing Philips XL-30 Scanning Electron Microscope (FEI Company, Netherlands). Each sample was covered with a thin film of carbon and sputter coated with gold. The microscope magnifications of fibers were 500x.

MECHANICAL TESTING OF THE FIBERS

For diameter and count number determinations in accordance with ISO 5084 (1996) [14] fiber samples were stored at 20 ± 2ºC and relative humidity of 65 ± 4% for 24 h. After acclimatization, each sample was weighed employing an analytical balance (AUW220D, Shimadzu, São Paulo, Brazil). The obtained results represent the rate between the weight and the fiber length [20]. The assay was carried out based on ISO 2060 (1994) [21], ISO 1139 (1973) [22] and ISO 139 (2005) [23]. Tensile properties of the acclimatized fibers (rupture strength, tenacity, elongation, and Young's modulus) were determined according to ASTM D 3822 (2007) [24] employing tester machine Instron (model 5569, Norwood-MA, USA). Formerly, to determinate tenacity (strength value shared by count number) fiber fineness (linear density or count number) was calculated in terms of TEX, defined as the weight in grams per 1,000 m of the fiber, by weighing a known length of the fiber. A load cell of 10 N, gauge length of 200 mm, automatic pre-tension and crosshead speed of 100 mm/min were employed. The tensile parameters were determined when the fiber broke immediately after maximum elongation.

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DIFFERENTIAL SCANNING CALORIMETRY – DSC/ THERMOGRAVIMETRY – TGA

DSC tests were performed in the DSC 7020 (Exstar, SII Nano Technology In., Japan) under an inert nitrogen atmosphere at a flow rate of 50 mL/min. Temperatures ranged from 25 – 350 °C with a heating rate of 10 °C/min. A closed aluminum capsule containing 2 mg of sample mass was used. The temperature and fusion heat were calibrated with Indium.

TG analysis was performed in a TG/DTA 7200 (Exstar, SII Nano Technology In., Japan) under a 100 mL/min^{-1} nitrogen atmosphere. Temperatures ranged from 25 – 600 ºC with heating rate of 10 ºC/min^{-1}. Closed platinum capsules containing 3.5 mg of sample mass were used. The temperature and heat fusion were calibrated with Calcium oxalate before the assay.

Both DSC and TG analyses were performed with alginate, chitosan, and hybrid fiber, without and with glycerol. The assays were performed at the Department of Pharmacy, School of Pharmaceutical Sciences.

CELL VIABILITY ASSAY

For analysis of cytotoxicity were used 0.5 g of samples of chitosan, alginate, and hybrid (alginate/chitosan) fibers. Samples were cut (about 0.5 cm) placed in vials of 12 mL and irradiated at 25 kGy.

The cytotoxicity tests were carried out employing NCTC clone 929 cell line from American Type Culture Collection (ATCC) (connective from mouse biological source, adherent growth mode, 2n = 40 karyotype, fibroblast morphology, suitable for cell culture), according to International Standardization Organization (ISO 10 993-5) [25] and the previously described methodology by Rogero et al. (2003) [26]. The extract obtained by sample immersion in cell culture medium MEM (Eagle`s minimum medium) for 24h was serially diluted and placed on 96-well microplates containing cell cultivations. The cytotoxicity effect was evaluated by reading the optical density at 540 nm (Tecan, Sunrise spectrophotometer, Männedorf, Switzerland) of neutral red uptake level. The cell viability percentage was calculated based on the control cells in the assay (100% viability). High-density polyethylene (HDPE) and 0.2% phenol solution in PBS were used as negative and positive controls respectively.

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VISCOSITY-AVERAGE MOLECULAR WEIGHT OF THE ALGINATE

The alginate and chitosan molar weight were not informed by the supplier, then the viscosity-average molecular weight was obtained by using the Mark-Houwink equation (Eq. (3)) [27].

$$[\eta]=KMv^{\alpha} \qquad \text{(Equation 3)}$$

The intrinsic viscosity [η] = 35.57 mL/g, at 25 ºC and alginate concentration of 5 g/ mL. The constants K = 0.0073 mL/g and α = 0.92 were used [28]. Finally, the viscosity-average molecular weight of the alginate was approximately 10196.43±204,89 g/mol. For chitosan the intrinsic viscosity [η] = 227,12 mL/g, 2%(g/mL) at 25 ºC [27,29]. The constants K = 4,74 x 10^{-3} mL/g and α = 0.73 were used [27]. The viscosity-average molecular weight of the chitosan was 15000 g/mol .

RESULTS AND DISCUSSION

WATER ABSORPTION AND WEIGHT LOSS

Important textile fiber properties are close relationships with fiber behavior in diverse atmospheric conditions. Most fibers are hygroscopic, i.e., they can absorb water vapor from a humid atmosphere and, conversely, lose water to a dry atmosphere. The absorbed water can influence many of the fiber's physical properties, such as dimensions, tensile strength, elastic recovery, electric resistance, toughness, etc. In the case of fabrics, the humidity exerts a hard influence on the adequacy and the purpose of a garment article [30]. The structural details determine the apparent behavior of the fiber. For example, in a fabric produced from hydrophobic fibers, such as polyester, the fibers and yarn surface can absorb water by capillary effect [30]. In the same way, a fabric with a determined cover factor (the ratio of fabric surface occupied by yarn to the total fabric surface) seems to be more absorbent than another with a lower value made from the same raw material.

The capacity of a material to retain water in its structure is a remarkable characteristic for applications in the medical area. For example, in dressings used in wounds with secretion, a fiber with high fluid absorption could remove this secretion, helping the healing process [31]. According to the application, the materials specifications for wound treatment (absorbance, tenacity, flexibility, softness, and in some cases, biostability and biodegradation) are essential [31,32] .

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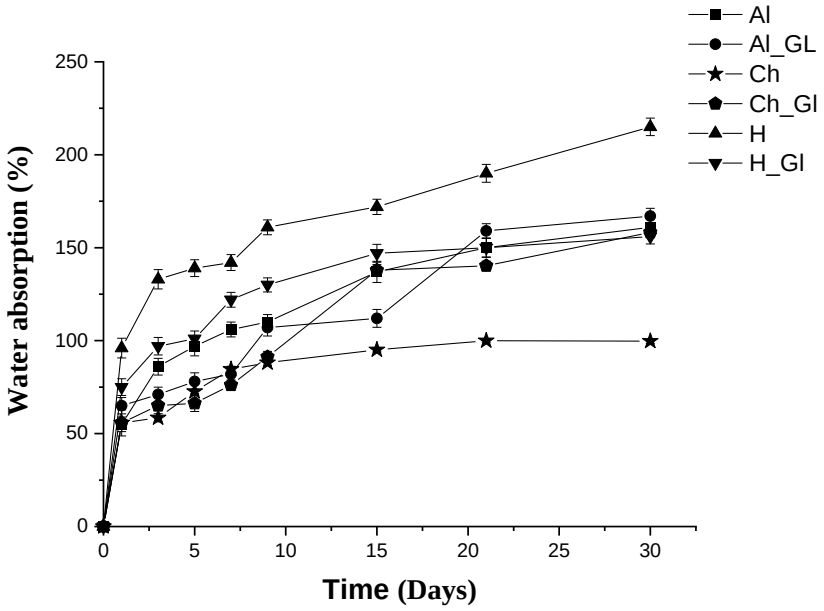
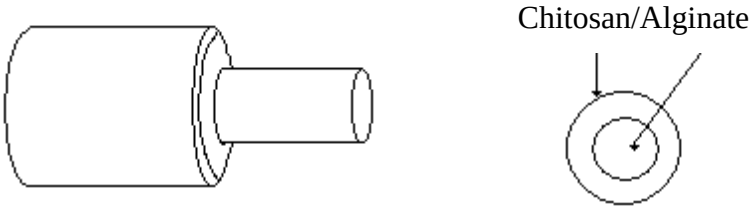
Figure 1 presents water absorption versus time for fibers prepared from alginate, chitosan gel and hybrids alginate/chitosan without and with glycerol. The absorptions in tests carried out for 30 days were: 161% for the alginate without, 167% for alginate with glycerol, 100% for chitosan, chitosan with glycerol 158% and 215% e 156% for the hybrid fibers without and with glycerol respectively.

Figure 1. Water absorption (%) versus time for AL (■), AGL (●), CH (★), CHGL (⬟), H(▲) and HGL (▼) fibers.



Alginate is a natural hydrophilic polymer and when it is used with chitosan polymer, the water absorption capacity of hybrid material increased in relation to the values of isolated compounds (Figure 2).

Figure 2. Alginate/chitosan hybrid fiber showing coating of chitosan on the alginate fiber.



In this case, the synergic interaction between the properties of both polymers implied a better water capacity absorption characteristic than from each isolated polymer. The

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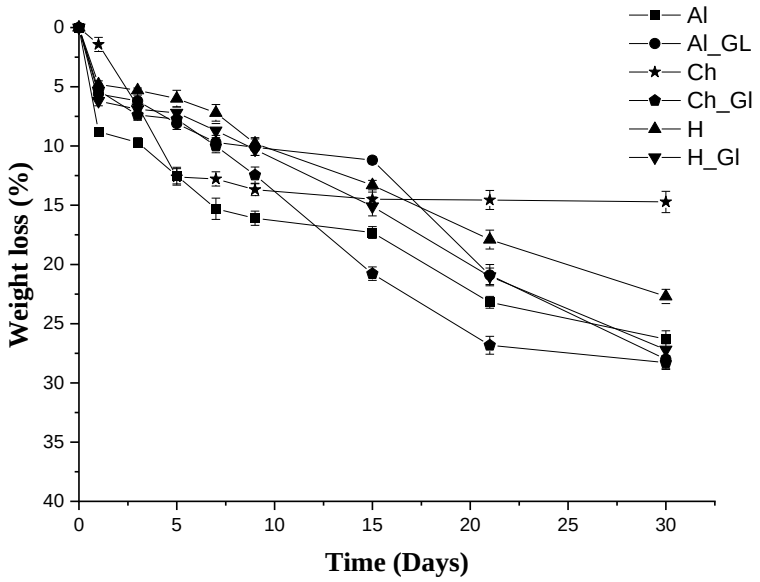
absorption of water in the fiber structure is a determining factor in the type of application of this material [31].

The weight loss was 28% for alginate fiber with glycerol, 8% increase compared to the mass loss of alginate fiber without glycerol. For the chitosan was 15% and chitosan with glycerol 28%. For the hybrid fibers with glycerol was detected a mass loss of 27% being 17% smaller compared to the hybrid fiber without glycerol (Figure 3).

Figure 3. Weight loss (%) versus time for AL (■), AGL (●), CH (★), CHGL (⬟), H (▲), HGL (▼) fibers.



The use of chitosan polymer increased the weight loss of the fibers, probably because of the biodegradable properties known of this biopolymer [33]. The use of glycerol increased the mass loss because it is alcohol possibly volatilized, contributing to potentiate weight loss over the days. Another point is the high presence of water molecules in the structure of the fiber with glycerol (which is probably lost during drying and therefore increases weight loss) justified by the presence of glycerol with the ability to attract more water molecules and consequently increase the absorption [34].

MORPHOLOGICAL ANALYSIS

Scanning electron microscopy (SEM) was used to evaluate the quality of the fibers since it allows the evaluation of encrustations, thicknesses, and irregularities along the fibers. In addition, it can determine fiber grouping, the presence of marks on its inside, the presence

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or not of marrow, the shape of transversal and longitudinal sections, and color differences, among others.

Figure 4. Scanning electron microscopy (SEM) images of fibers obtained with glycerol (left column) and without glycerol (right column) respective fibers of: (a, b) alginate; (c, d) chitosan; and (e, f) hybrid.

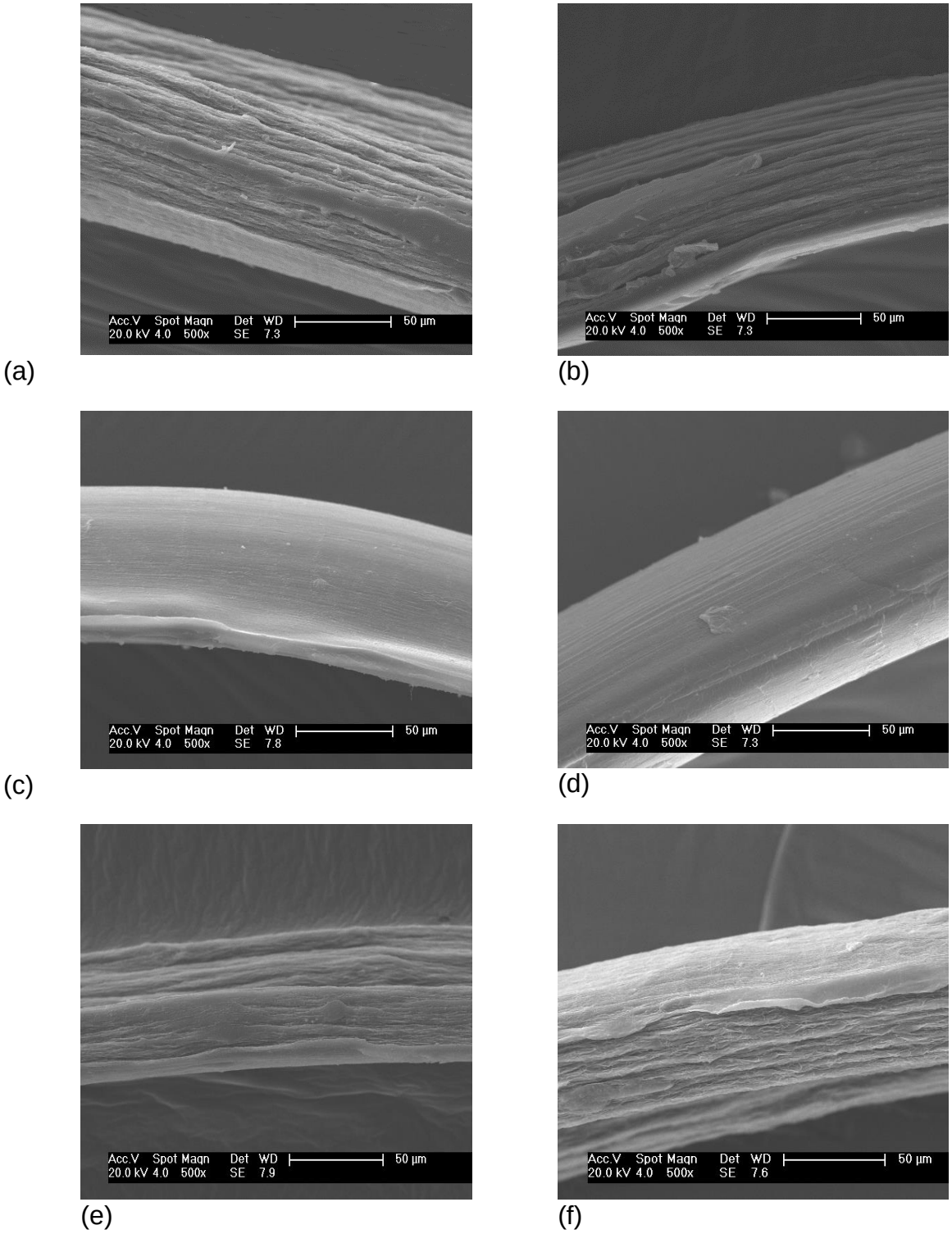

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Figure 4 shows SEM images of fibers made from alginate (Figure 4a and 4b), chitosan (Figure 4c and 4d), hybrid (Figure 4e and 4f) with and without glycerol. It is observed that fibers are oriented in the longitudinal direction, presenting uniformity even considering the manual extrusion process for their production. It is also possible to observe the presence of heavy longitudinal striations on the surfaces of all fibers (Figure 4), probably due the manual extrusion process. For the extraction was used a syringe cut manually. With other cutting methods, such as laser cutting, these striations could be avoided.

In the hybrids fibers it is observed the presence of chitosan on the coating surface of alginate fibers (Figures 4d and 4e), demonstrating that the employed process was effective.

Alginates can gel via two mechanisms: ion dependently and ion independently. The ion dependent mechanism occurs at pH values above the pKa of alginate, the pKa of alginate lies between 3.38 and 3.65, and in the presence of divalent cations such as calcium ions (Ca^{2+}). Under these conditions bound sodium ions are exchanged with calcium ions, in solution, which causes the dimerization of adjacent alginate chains, forming a three-dimensional, hydrophilic, and yet insoluble network [14,35].

Chitosan, the other prevalent natural polysaccharide is the partially N-deacetylated derivative of chitin. The amino group in chitosan has a pKa value of ~6.5, which leads to a protonation in acidic to neutral solution with a charge density dependent on pH and the %DA-value. This makes chitosan water soluble and a bioadhesive which readily binds to negatively charged surfaces such as mucosal membranes. Polyelectrolyte complexation can occur between alginate and chitosan as they are oppositely charged polysaccharides; alginate is polyanionic and chitosan is poly cationic. However, this interaction is dependent on the local pH [36].

As showed in Figures 4 for all produced fibers the average diameter is in the range of 75-100 µm. The fineness or diameter of fibers is an important property. It influences the functional characteristics of fibers, yarns, fabrics, knits, and nonwovens [20]. In this work were produced and characterized fibers in micrometric order of magnitude. It is possible to consider that by diminishing this order of magnitude until the nanometric scale, these properties could be potentiated, besides the possibility of reducing costs by employing less material. Of course, this hypothesis will be proved by analysis of results from further studies.

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TENSILE TESTS

For performing tensile tests, generally, fiber diameter is estimated by an indirect measurement known as count number. The usual indication form of the count number of fibers is TEX, which is defined as grams per 1000 meters of fiber.

Table 1. Results of tensile tests. The values are expressed of average of 20 determinations on acclimatized fibers (20ºC, 65% relative humidity), respective standard deviation and variation coefficient.

Fibers	Count number (tex)	Breaking load (N)	Tenacity (cN/tex)	Elongation (%)	Young´s Modulus (N/tex)
Alginate (Al)	27.6 ± 1.34	1.62 ± 0.11	7.25 ± 0.52	4.89 ± 2.43	4.77 ± 0.49
Alginate (AlGl)	29.2 ± 1.39	1.35 ± 0.07	7.75 ± 0.44	6.08 ± 1.85	5.02 ± 0.47
Chitosan (Ch)	17.2 ± 0.7	0.77 ± 0.05	4.47 ± 0.28	1.45 ± 0.97	4.16 ± 1.01
Chitosan (ChGl)	17.2 ± 0.65	1.49 ± 0.08	8.64 ± 0.51	4.25 ± 0.83	5.55 ± 0.41
Hybrid (H)	18.4 ± 0.82	1.64 ± 0.10	8.89 ± 0.55	5.44 ± 2.4	5.66 ± 0.77
Hybrid (HGl)	15.1 ± 0.79	1.53 ± 0.05	10.0 ± 0.33	6.17 ± 1.93	5.72 ± 0.54

Table 1 shows count number (tex), breaking load (N), tenacity (cN/tex), elongation (%) and Young´s modulus (N/tex) results to the different types of alginate and hybrid fibers produced. The fiber produced with the alginate gel presented the opposite behavior, i.e., when glycerol was employed, the count number increased. Considering that all fibers have the same diameter range as evidenced by SEM analysis, these significant differences could be associated with a variation in the densities of fibers provoked by the different processes which were employed for their respective production.

Fiber tenacity is the quotient of breaking load by the count number. This calculation is necessary to normalize the effect of different thickness values found in some samples containing several fibers [20]. Table 1 shows the tenacity values of all alginate fibers were very similar.

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The influence of glycerol as a plasticizer agent was observed in elongation results. The Alginate (GL) fibers showed elongation values 19.6% greater than for alginate. Tenacity values for alginate and hybrid fibers were between 7.25-7.75 and 8.89-10.0 cN/tex, and the employment of glycerol is associated with a trend to increase the tenacity values. The tenacity values obtained in the present study are slightly inferior to the values found in the literature (14.0-18 cN/Tex) [37] and (11.0-18 cN/Tex) [37,38]. However, it is worth of mention that the cited references do not mention the polymer concentration employed in their determinations.

The produced fibers from alginate and hybrid ones could be considered brittle considering their tenacity values and thinking in textile applications when, for example, these values are compared with cotton tenacity ones (26.5-43.3 cN/tex) [39]. However, the of Young´s modulus of produced fibers (4.9-6.2 N/tex) is compatible with cotton values (5.4-6.2 N/tex) [39,40] indicating some similarity between these fibers about stiffness and mechanical resistance.

Traditionally wound dressings are made of cellulosic fibers such as cotton and viscose rayon fibers in the form of woven or nonwoven gauze. These bandages are highly absorbent and considering that fiber structure is chemically, physically, and biomedical inert to the wound healing environment, the fibers remain integral while the treatment. Upon healing of the wound, the dressing and fibers can be adhered with the dry scar, and bandage removal sometimes becomes painful and traumatic [41,42].

In this way, another possible strategy could be to produce a two-layer woven or nonwoven fabric, one for providing fabric resistance and the other one to contact the skin, which could alleviate the pain, absorb exudates, and curb bleeding. It is noteworthy that changing the water absorption it is possible to increase or decrease the degradation of materials. Thus, the time of application or duration of this material in the wound could be determined by the alginate/chitosan fiber content taking into consideration its water absorption property.

Alginate and chitosan are polymers very applied in biomaterials. Separately both ones can absorb water and degrade themselves. Despite of the water absorption characteristic of alginate, its contact whit exudates benefit bacterial proliferation [41]. In this way chitosan added in hybrid fiber could bring the advantages relative to biodegradability, bactericidal, fungicidal, and healing properties [33,41]. Further studies must be done to determine these properties and develop a product suitable for medical applications.

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The fabric matrix structure (or the scaffold) is also important for medical applications [14]. In addition, as observed earlier in this study, the fibers were produced in micrometric order of magnitude, presenting a set of properties reported here. It is possible to consider that by diminishing this order of magnitude until the nanometric scale, these properties could be potentiated, besides the possibility of reducing costs by employing less material. In this way, electrospinning has emerged as one of the most versatile processes to produce fibers with submicron and nano diameters from a wide range of polymers. Biodegradable polymeric electrospun nanofiber matrices (scaffolds) are attracting significant attention for various biomedical applications including tissue engineering [43,44]. Thus alginate/chitosan polymers could be their biomedical characteristics improved by the electrospinning nanotechnology employment.

DIFFERENTIAL SCANNING CALORIMETRY – DSC/ THERMOGRAVIMETRY – TGA

Differential Scanning Calorimetry is an important study of a material thermal behavior that identifies mass loss, reduction reactions and desorption by the endothermic peaks and crystallization, polymerization reactions and oxidation by the exothermic peaks [45]. The results of the DSC of the fibers with and without glycerol are presented in the Table 2.

The chitosan fibers with and without glycerol present similar DSC curves (Figure 5) with two events, the first relates to the evaporation of absorbed water and the second is polymer degradation (degradation of the saccharide ring, depolymerization and decomposition of acetylated and deacetylated chitosan units) [46].

Table 2. Results from DSC analysis of chitosan, alginate and hybrid fibers with and without glycerol.

FIBER	EVENT	T_{ONSET} (ºC)	T_{OFFSET} (ºC)	T_{PEAK} (ºC)	ΔH (mJ mg-1)
Chitosan	Endothermic	60.28	250.41	180.85	-45974.52
	Exothermic	269.71	344.53	303.86	25660.18
Chitosan with glycerol	Endothermic	63.35	182.78	118.34	-45691.90
	Exothermic	277.71	344.49	302.43	29450.13
Alginate	Endothermic	87.59	192.99	122.70	-70065.32
	Endothermic	193.24	212.99	195.79	-5261.46
	Exothermic	227.13	344.18	267.93	22802.90
Alginate with glycerol	Endothermic	98.40	215.22	178.54	-112739.30
	Exothermic	215.22	344.57	271.78	59913.65
Hybrid	Endothermic	118.88	216.39	174.32	-55536.60
	Exothermic	216.14	344.45	275.61	27863.68
Hybrid with glycerol	Endothermic	146.84	224.23	173.85	-57446.57
	Exothermic	226.83	336.15	276.30	20516.48

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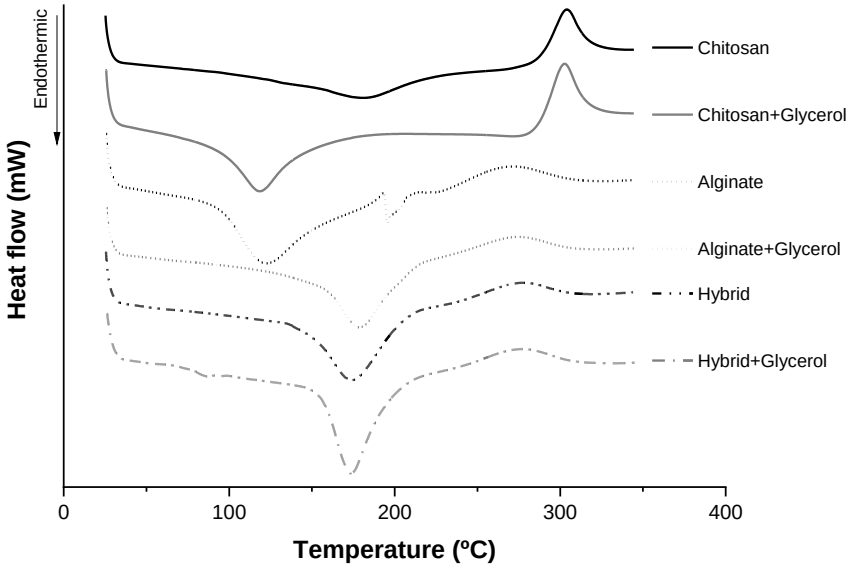
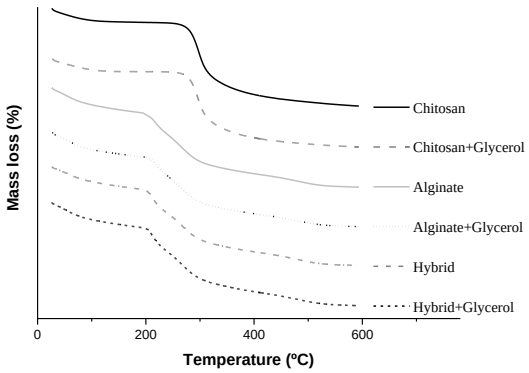
Figure 5. DSC of chitosan, alginate, and hybrid fibers without and with glycerol.



The alginate fibers with no glycerol showed three events, the first endothermic event can be occurred due to water evaporation, the second was an endothermic event and it can be attributed to the polymer melting point. Finally, the third exothermic event can be explained by the polymer degradation [47]. The alginate fibers with glycerol showed only two principal events (Table 2) resulting of increase in the polymer melting point and the polymer degradation temperatures due to the glycerol presence. The hybrid fibers with and without glycerol similar behavior to the alginate DSC curves (Fig. 5) but only two different thermal events, it can be due to no interaction between alginate and chitosan. A completely miscible mixture of two polymers is characterized by an intermediate temperature between the two polymers that compose it [48].

Figure 6. Comparative TG of alginate, chitosan, and hybrid fibers without and with glycerol.



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The thermogram Figura 6 showed similar behavior of the alginate and hybrid fiber with and without glycerol, presenting three mass losses about water evaporation and polymer degradation. The chitosan fiber with and without glycerol presented two mass losses associated with the dehydration process of saccharide rings, decomposition of acetylated and deacetylated units of chitosan and depolymerization [46].

Considering the possibility of thermolability, the option of fibers produced without glycerol is more attractive due to the increase in heat resistance. This is important for the medical dressing sterilization produced with this raw material. The most common hospital sterilization of textiles is carried out at 121°C for 30 or more minutes. In some cases, such as surgical textiles, irradiation is also commonly employed, but this technique is more complex and expensive.

Table 3. Results from TGA analysis of chitosan, alginate, and hybrid fibers with and without glycerol.

FIBER	MASS LOSS EVENT	T_i (ºC)	T_f (ºC)	MASS LOSS (%)
Chitosan	1	30.96	142.22	7.2
	2	244.63	491.17	50.45
Alginate	1	26.79	153.89	14.2
	2	206.60	463.63	40.26
	3	463.63	591.50	5.03
Chitosan with glycerol	1	28.44	155.44	7.68
	2	244.83	581.30	48.09
Alginate with glycerol	1	35.15	99.11	8.92
	2	192.39	426.50	37.97
	3	426.50	578.19	6.82
Hybrid	1	33.8	105.69	8.54
	2	191.36	428.96	41.74
	3	428.96	580.27	7.13
Hybrid with glycerol	1	36.18	101.28	8.97
	2	186.37	433.78	43.36
	3	433.78	587.41	7.06

CYTOTOXICITY TESTS

For cytotoxicity tests, the cell viability percentages were plotted against extract concentration (in percentage) resulting in cellular viability curves shown in Figure 7. In this analysis, the curves above 50% cell viability (cytotoxicity index line = IC50%) are considered noncytotoxic and those below or crossing the IC50% line are considered cytotoxic [49,50].

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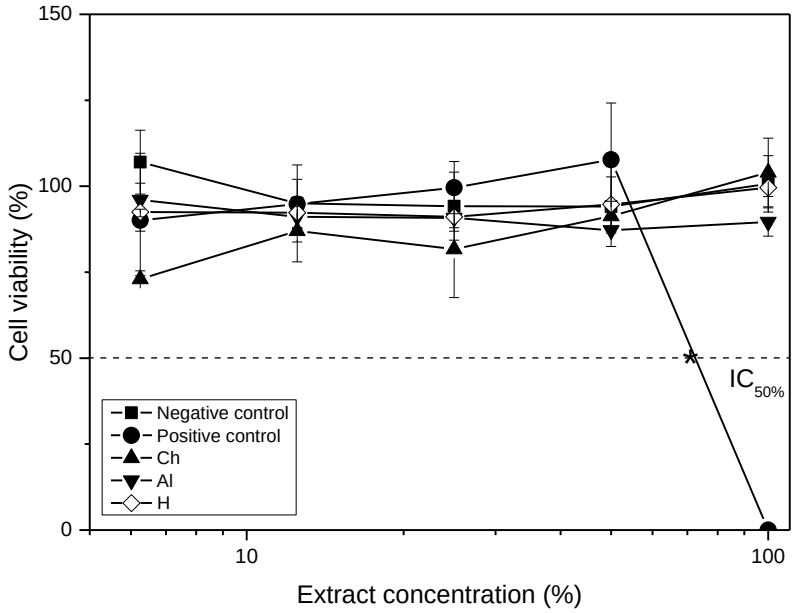
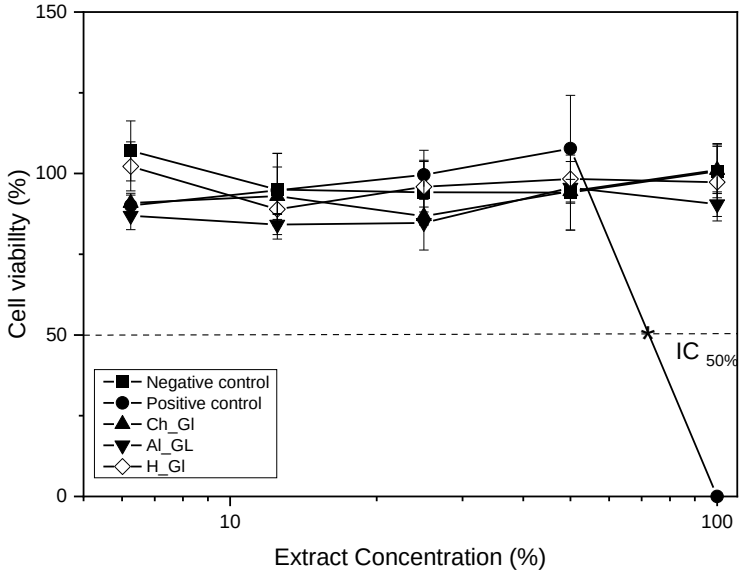
Figure 7. (a) Cell viability curves in fibers without glycerol obtained from chitosan (-▲-), alginate (-▼-), hybrid (alginate/chitosan) (-◊-), negative control (-■-) and positive control (-●-). (b) Cell viability curves in fibers with glycerol obtained from chitosan (-▲-), alginate (-▼-), hybrid (alginate/chitosan) (-◊-), negative control (-■-) and positive control cytotoxicity test (-●-).



(a)



(b)

All chitosan, alginate, and hybrid fibers without (Figure 7a) and with glycerol (Figure 7b) did not show cytotoxicity considering the negative control curve from 0 to 100% of the

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extract concentration. This indicates that the employment of these fibers could be safe in direct contact with other animal cells, including human ones.

Therefore, the results obtained in the present study are promising for using chitosan and alginate as raw materials to produce textile hybrid fibers and their use in biomedical applications. New studies will be carried out to improve the fiber and fabric production processes.

CONCLUSION

In this study fibers from biopolymers of alginate and hybrid of alginate/chitosan were developed. Different methods to produce alginate gels with glycerol were tested. The produced fibers were evaluated in function of water absorption or swelling, weight loss, tensile properties, and cytotoxicity. The water absorption was increased with the glycerol addition for alginate and chitosan fibers. For hybrid fibers the glycerol did not benefit water absorption. The weight loss increased with the glycerol addition for all fiber tested. Tenacity values for alginate and hybrid fibers were between 7.25-7.75 and 8.89-10.0 cN/tex, and the employment of glycerol is associated with a trend to decrease the tenacity values. All fibers of chitosan, alginate, and hybrid fibers without and with glycerol showed no cytotoxicity. The results obtained in the present study are promising for chitosan and alginate employment as raw materials for textile fiber production and biomedical applications. New studies will be carried out to improve the fiber and fabric production processes.

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