Corona Discharge Treatments of Plastified PVC Samples Used in Biological Environment

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ABSTRACT: The effects of the plasticizer content and of the treatments by corona discharge in helium on the morphology and on some physico-chemical properties of the PVC surface were investigated by scanning electron microscopy (SEM), IR spectroscopy, and contact angle measurements. A biological test of adsorption of some ions (calcium, potassium, and sodium) from human serum sanguine on the surface of PVC was also performed. After corona discharge treatment, the surface morphology presents a cleaning of oligomers and an increase in porosity, depending on the treatment time and on the content of the plasticizer. Surface energy considerably increases and functionalization of the surface is observed after treatment by corona discharge in helium. This functionalization does not change the electrolitical equilibrium of some ions from the serum sanguine, a convenient result that controls the stability of the blood-PVC sample interface. © 2001 John Wiley & Sons, Inc. J Appl Polym Sci 81: 2419–2425, 2001

Key words: corona discharge treatment; plastified PVC samples; surface properties; biological environment

INTRODUCTION

Materials used in medical applications, including those used in biological environments, must have specific mechanical, physico-chemical, and biological properties, and, in many situations, the surface properties are different from the bulk properties. These materials should not cause thrombosis, alterations of plasma proteins (albumin, globulins, fibrinogen, etc.), destruction of enzymes or of cellular elements of the blood, adverse immune responses, or toxic or allergic reactions.[1]

In order to obtain polymers with the properties required for medical applications, different types of additives, such as plasticizers, antistatics, fillers, stabilizers for UV and heat, etc., are used. Usually, these additives migrate to the surface, producing changes in the properties and instability of the surface characteristics. In this respect, it is important to modify the physico-chemical properties of the polymeric surfaces in order to make them useful for long term biomedical applications.[2,3,4]

Poly(vinylchloride) (PVC) is one of the materials most used in medical applications. PVC has many desirable properties, such as flexibility, kink resistance, toughness, chemical and biological resistance, and suitability for sterilization by EtO, gamma irradiation (with no discoloration), or by autoclave. Furthermore, PVC surfaces present the lowest adhesion of bacterial cells among 10 different plastic materials, including polyethylene and silicone.[5,6]

PVC is used in medical devices and implants, and to store blood and blood products, drugs, injectables, etc. The flexibility of the material is important in these applications, this property being particularly influenced by the type and amount of plasticizer used in the PVC. The type and amount of plasticizer can modify not only the

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flexibility, but also some other properties of PVC samples, such as tensile strength, toughness, permeability of gases and water, etc. Plasticization usually increases the permeability of gases due to the increased molecular mobility of local polymeric chains at the polymer-air interface. In medical applications this behavior is important, as PVC is used for storing substances that are affected by permeating gases.[7]

Generally, during sterilization, these materials can change their physico-chemical and mechanical surface properties. For instance, exposure to gamma radiation has a negative effect on PVC samples; immediately after sterilization the material tends to turn yellow or dark. One way to improve the gamma radiation stability is to choose the resin, stabilizer, lubricant, antioxidant, or the plasticizer loadings. An increased concentration of plasticizer significantly reduces the yellowness index of the material after gamma sterilization.[5,6]

In medical applications, the biological liquids are able to extract monomeric plasticizers from PVC, producing changes in their properties and possible toxic and biological effects. In many situations, there may be a transfer of plasticizer to the patient, with possible long term effects.[5,6]

Thorough research must be performed in order to solve the two problems. The physico-chemical modifications of the surface properties must create a barrier to any in-out mass transfer and supplementary they have to remain within the ranges required for medical applications.

Many methods are known that can be used to obtain the required properties, and one of these is to modify the polymeric surface by plasma treatments.[2,3,8,9] These modifications include wettability, biocompatibility, resistance to biological degradation processes, etc. In order to obtain modifications of the surface properties that satisfy the biological requirements, corona discharge treatments are used due to advantages such as: simplicity, ability to work at atmospheric pressure, less expensive processing, dry technology, etc.[8,9]

Taking into account the above-mentioned aspects, the purpose of this work was to study the effects of the plasticizer content and of the treatments by corona discharge on the morphology and on some physico-chemical properties of the PVC surface. Our results emphasize that the selection of the corona discharge parameters and of the working gas (helium) seems to be particularly suitable to generate beneficent influences upon the treated surface properties. Investigations were made by correlation of the morphology, surface energy, chemical structure, and biological response of treated samples. New physical and chemical reactivity of PVC samples were shown to be acquired. Moreover, this new functionalization of the surface created by corona discharge treatments allows for the control of the stability of the blood-PVC sample interface, a convenient result for selection of the polymeric material for biomedical applications.

EXPERIMENTAL

PVC surface treatments were performed by using a corona discharge in helium, produced by a generator with variable frequency, amplitude, and polarity of electrical pulses.[8,9] A plasma beam was produced by ionization of the gas, which flowed in a glass tube (Fig. 1). High tension pulses were applied by an electric generator, power 40 W, 10 kV of amplitude, 1300 Hz of frequency, and 40 μs of length. The gas flow was 300 cm^3/min. The discharge was working in a point-to-plane geometry, at atmospheric pressure. The plasma beam thus formed allowed for local surface treatment.

Some surface properties of PVC were investigated before and after plasma treatment. Time of treatment was either 10 s or 1 min.

In this experiment, the plasticizer (diethyl hexylphtalate) content of PVC was modified, but the amount of all other compounds remained constant, e.g., hydrophylization additives, stabilizers, etc. One mm thick PVC samples with two different contents of plasticizers (100% PVC, 50% diethyl hexylphtalate, 3% stabilizer and 100% PVC, 75% diethyl hexylphtalate, 3% stabilizer) were used.

The effects of corona discharge treatments of PVC surfaces on the morphology and on some physico-chemical and biological properties of the surface were investigated by scanning electron microscopy (SEM), Fourier transform infrared spectroscopy in attenuated total reflectance mode (FTIR-ATR), and contact angle measurements. Micrographs were obtained using a Tesla 340BS electron microscope, operating at 25 kV, on PVC samples covered by thermal sputtering with a thin (about 20 nm) silver layer. Absorbency spectra were recorded using a Bomem spectrophotometer of 2 cm^{-1} resolution and by coaddition of 100 scans. Contact angles were measured by the sessile drop technique.

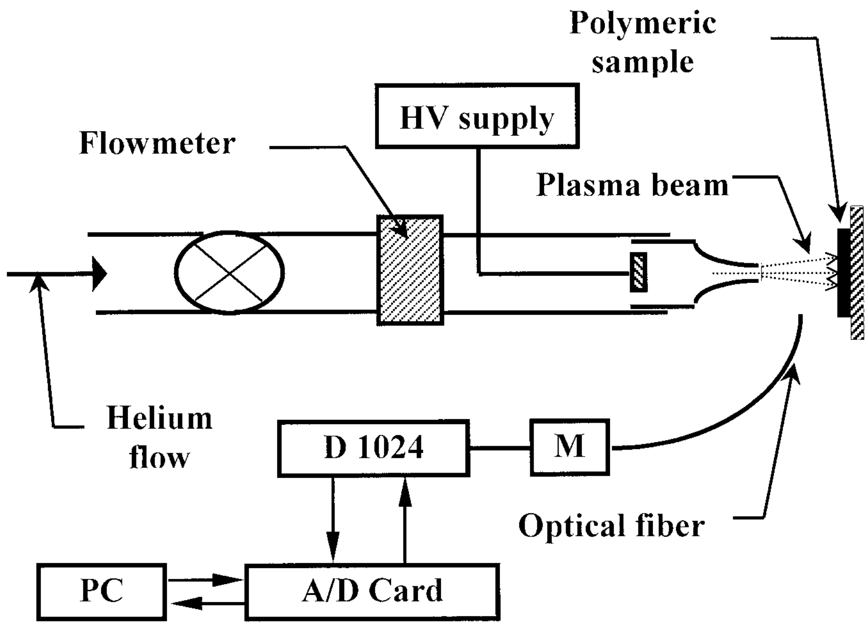

Figure 1 Experimental set up.

In order to measure the adsorption of some ions (calcium, potassium, and sodium) as a biological test, we exposed treated PVC surfaces to human serum sanguine. PVC surfaces were exposed to serum sanguine for 1 h, 1 day, 2 days, or 7 days, at the constant temperature of 25°C. Ion concentrations in serum sanguine were measured with an analyzer type AVL 984-S, and the pH of the serum was controlled in all experiments with a Beckam ϕ300 pH-meter.

RESULTS AND DISCUSSION

Surface Morphology

After corona discharge treatment, the surface morphology presented significant alterations. Figure 2 illustrates the influence of treatment time on the surface morphology of PVC samples containing 50% plasticizer.

A cleaning effect of the surface takes place by removal of oligomers and adsorbed contaminants [Fig. 2(b)]. This is an important effect of the discharge, which not only creates a clean surface, but also allows further direct reactions on the polymeric chains. Removal of the oligomers is beneficial, because oligomers promote cancerogen effects in tissues surrounding medical implants. An ablation of the amorphous polymer regions is probably many times faster than that of the crystalline polymeric material.

The appearance of micropores (microroughness) and an increase of their density on the surface depends on the treatment time [Fig. 2(c)]. These new micropores may lead to an increase in the area available for adhesion phenomena, as well as to creation of a new functionality on the surface via formation of volatile reaction products and molecular fragments.

Similar features were obtained for the surface morphology of PVC samples containing 75% plasticizer.

This new morphology is important for medical applications, because adhesion, growth, and proliferation of endothelial cells, as well as anticoagulant implant properties depend not only on the chemistry, but also on the surface morphology.

Functionalization of the Surface

Some modifications of the chemical properties, particularly the formation and/or decomposition of new radicals on the surface after corona discharge treatment, were shown by means of FTIR-ATR spectroscopy.

In Figure 3, ATR-IR spectra of untreated and treated samples are presented. All of these spectra are a superposition of pure PVC and plasticizer spectra. Therefore, the principal peaks that

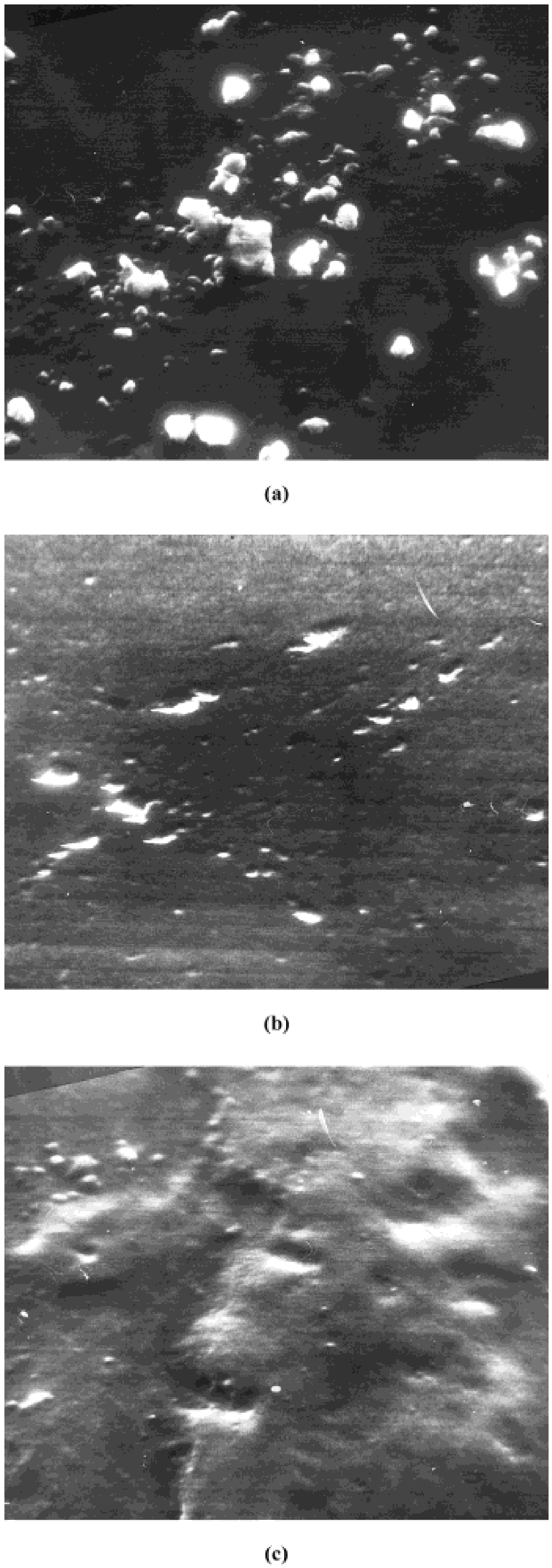

Figure 2 SEM images (×6000) of PVC samples with 50% plasticizer: (a) untreated sample, (b) 10 s treated sample, (c) 1 min treated sample.

appear in the PVC spectra, in the 500–4000 cm^{-1} range are the following: at 616 and 670 cm^{-1} due to C—Cl bonds, at 1000–1250 cm^{-1} due to C—C or C—O bonds, at 1460 cm^{-1} due to CH_2 of radicals, at 1620 cm^{-1} due to amorphous carbon C═C, at 1720 cm^{-1} due to C═O bonds, at 3390 cm^{-1} due to formation of OH radicals.

Differences between untreated and treated samples were not significant because the treatment by corona discharge induced modifications of a surface layer that was not thick enough (about 50 Å) to induce detectable changes of IR spectra. However, the presence of functional groups containing OH (3390 cm^{-1}) was increased after corona treatment of the surface. These OH groups may be introduced onto the surface by interaction of the activated PVC surface with atmospheric oxygen and/or directly by corona discharge treatment. Treatments in helium at atmospheric pressure, flowing of gas at the outlet of the tube was accompanied by air entraining in the beam, which thereby was formed by an He-air mixture.[10] In this mixture, oxygen was likely to make an important contribution to the surface modification. This result is important for medical applications of PVC samples, because the polymeric surfaces contain more hydroxyl groups and thus they are favorable to attachment and growth of cells.[11,12]

Corona discharge treatment can induce surface functionalization not only by generation of polar groups, such as OH groups, but also by rearrangements of active sites on the surface, with further consequences for the interfacial energy air-PVC surface.[12] In order to estimate the new functionality induced by corona treatment, contact angle measurements were employed.

Surface energy considerably increased because the treatments provided new functional groups on the surface. In this respect, the polar component of the surface energy showed an important increase after treatment, while the disperse component presented only a small variation, as compared to the untreated sample (Table I). Functionalization of the treated surfaces was thus improved, as low dispersion and high polarity of the surface can be used for further linkages on the surface.

Surface wettability is an important characteristic that affects biocompatibility by preferential adsorption and retention of some proteins from blood plasma. Thus, it has been found that a decrease of the wettability leads both to significantly less fibronectin (one of blood plasma pro-

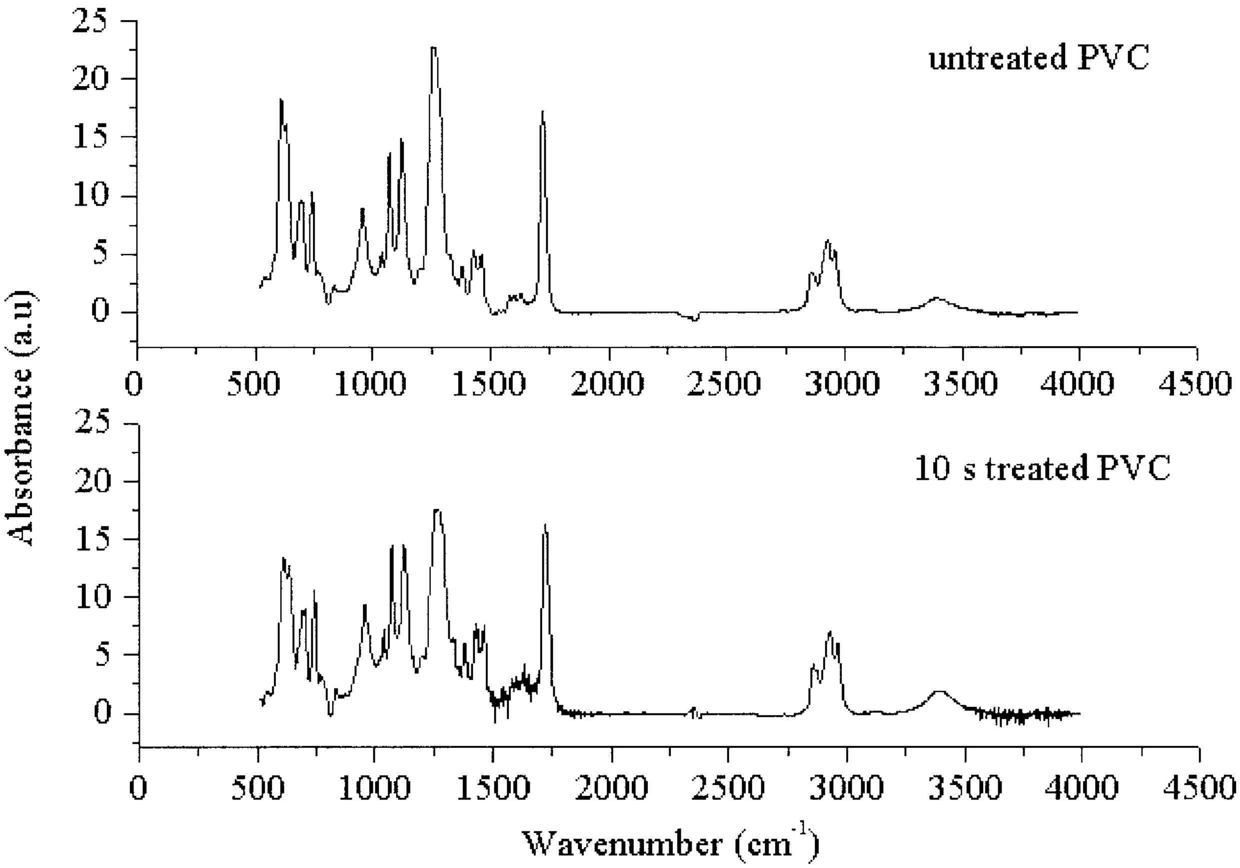

Figure 3 ATR-IR spectra of PVC samples with 50% plasticizer.

teins) deposition, and, in addition, to severe modifications of adsorbed cell morphology.[11] In this respect, the adhesion work (W_a) of water on the treated surface was measured, taking into account that blood plasma contains more than 60% water. Measurements of W_a as a function of ageing time show practically constant values for the sample that contains 50% of plasticizer (Fig. 4). This behavior allows for stabilize biocompatibility properties of the material.

Biological Test Results

The electrokinetic processes at the treated surface-blood interface were evaluated by a test of ion adhesion on the surface. It is a sensitive test that indicates changes in the functionality of the surface, and, in particular, it emphasizes the presence of polar components on the surface.

When introducing a polymeric material into a biological environment, an exchange of electrical

Table I Polar (γ_s^p) and Disperse (γ_s^d) Components of the Surface Energy (m*N*/m) of PVC Samples

PVC		Untreated	Treated 3 H	1 Day	15 Days	30 Days
+ 50% plasticizer	γ_s^d	11.2	14.5	15.3	11.3	14.6
	γ_s^p	12.0	27.5	25.3	22.9	21.5
+75% plasticizer	γ_s^d	14.6	11.4	14.7	16	15.2
	γ_s^p	11.4	34.2	21.6	19.2	13.2

Treatment time 10 s.

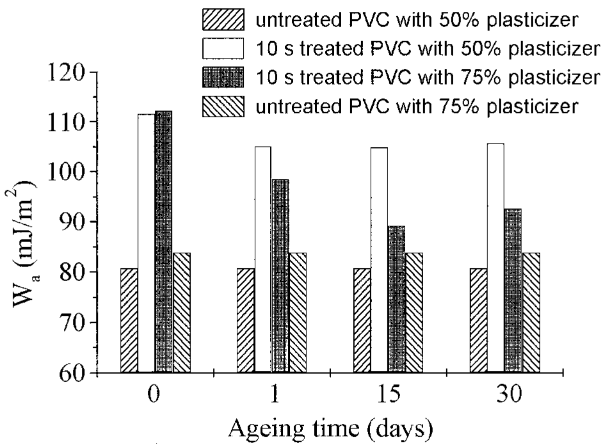

Figure 4 Surface energy of PVC samples, as a function of the plasticizer content and the ageing time.

charges has to be expected, and thus it may appear, at equilibrium, to have an electrical double layer (DL). By a permanent ion migration in and out and vice versa, a dynamic equilibrium at interface is maintained, and thus, these DLs may play a significant role in the initiation, prevention, evolution, and localization of intravascular thrombosis.

Blood was drawn from adult human donors into the test system (without anticoagulant), and serum sanguine (fibrin formed was removed) was separated from cellular elements by centrifugation in density gradient. Polymeric samples of PVC, 1 mm in thickness, in sheet form (1 × 2 cm^2), smooth, homogeneous, and without imperfections were exposed to serum sanguine for 1 h, 1 day, 2 days, or 7 days. The pH of serum sanguine was measured in all experiments.

PVC samples (untreated and treated) immersed in human serum sanguine (at 25°C) induced no modification of ion concentrations (sodium, potassium, and calcium), even after several days (Table II and III). Ion concentration values were maintained in the range of normal values, and similar results were obtained with the two types of PVC samples (with 50 and 75% plasticizer). In all experiments, the pH of the plasma sanguine was measured with satisfactory precision (0.01), and it was practically constant (7.4–7.6).

These preliminary results are important, but further biological tests should be done, in particular measurements of the zeta potentials, for a better understanding of the processes occurring at blood-grafting material interfaces.

CONCLUSIONS

Corona discharge treatments are a common method used to improve the wettability, adhesion, and biocompatibility of the polymeric surface, without affecting the bulk properties. Treatments of PVC by corona discharge in helium particularly offer the possibility for modification of the surface characteristics (morphology, wettability, functionalization, bonding, and interfacial adhesion with the biological environment) towards the ranges required for medical applications. In treated PVC, the type and amount of plasticizers have an important influence on the new surface properties.

After corona treatment of PVC samples, the surface morphology presented a cleaning and an ablation of the amorphous regions, as well as an increase in pore density, depending on the treatment time and on the content of the plasticizers. These new pores may act as "activating sites" on the treated surface.

Also, an increased amount of functional groups of hydroxyl was detected on the surface as a result of treatment. Surface energy consid-

Table II Ion Concentrations in Blood Plasma, in mmol/L

	0 Days			1 Day			4 Days			7 Days		
Ion	A	B	C	A	B	C	A	B	C	A	B	C
Na^+	138	139	139	138	139	139	139	140	140	141	141	141
K^+	4.7	4.8	4.8	4.7	4.8	4.8	4.7	4.8	4.8	4.8	4.8	4.8
Ca^{++}	1.10	1.15	1.14	1.11	1.14	1.14	1.11	1.15	1.14	1.13	1.17	1.15

(A) Without PVC.
(B) With untreated PVC sample with 50% plasticizer.
(C) With 10 s treated PVC sample with 50% plasticizer.

Table III Ion Concentrations in Blood Plasma, in mmol/L

	0 Days			1 Day			4 Days			7 Days		
Ion	A	B	C	A	B	C	A	B	C	A	B	C
Na^+	134	134.1	134.1	135.5	135.9	138	134.1	134.6	134.4	134	134.3	134.4
K^+	4.2	4.2	4.2	4.13	4.14	4.13	4.07	4.12	4.00	4.10	4.08	4.11
Ca^{++}	1.10	1.10	1.10	1.33	1.34	1.35	1.22	1.27	1.29	1.30	1.31	1.32

(A) Without PVC.
(B) With untreated PVC sample with 75% plasticizer.
(C) With 10 s treated PVC sample with 75% plasticizer.

erably increased and functionalization of the surface was obtained after treatment by corona discharge in helium. Therefore, new physical and chemical reactivity of PVC samples was acquired. Functionalization of the polymeric surface exposed to the discharge may have acted as a barrier layer, hindering the diffusion of additives from the bulk of the polymer sample to the surface.

This new functionalization of the surface created by corona discharge treatments did not change the electrolitical equilibrium of some ions (calcium, sodium, and potassium) or the physiological pH of serum sanguine. This is a convenient result to control the stability of blood-PVC sample interfaces, and finally, the process of vascular homeostasis. Further investigations will be made to correlate the morphology, surface energy, chemical structure, and biological response of treated samples, in order to select polymeric materials for use in biomedical applications.

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