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Photopolymerizable hybrid sol gel coating as a barrier against plasticizer release

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ABSTRACT

In this work, a dip-coating method was applied to coat polyvinyl chloride (PVC) used in the field of medicine with an organic/inorganic sol gel hybrid layer based on two organic functionalized titanium alkoxide and organic grafted alkoxy silane. The aim of the coating is to prevent the plasticizers release from PVC and to protect PVC against UV degradation. The optical and structural properties of the coating were investigated using UV–visible and infrared spectroscopy. ATR-FTIR spectroscopy was performed to control the amount of plasticizer leaching from the PVC medical device. The mechanical properties of the PVC and coated PVC samples were determined using tensile test. The barrier effect of the hybrid sol gel on the migration of the plasticizers was assessed using high performance liquid chromatography. Surprisingly the coating protects the PVC substrate against the UVA degradation and prevents leaching of plasticizers up to 98%. The adhesion of the hybrid coating on PVC exhibits a constant value whatever the treatments (UV-ozone and plasma) performed on the polymer surface.

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1. Introduction

Polymers are commonly used in everyday life. Polyethylene terephthalate (PET) is used in packaging and polyvinyl chloride (PVC) is commonly used in medical devices. In general they are a low-cost polymer that exhibits excellent optical and mechanical properties. Unfortunately, exposing those polymers to the environment (UV radiation in air) changes its external appearance, modifies its surface, and degrades its properties [1,2]. PVC is used in the field of medicine especially in the area of infusion. Plasticizers like phthalates are incorporated into polyvinyl chloride (PVC) to ensure flexibility. These plasticizers are not covalently bound to PVC and thus migrate from the medical device to the infused solutions and come into contact with the patient [3–5]. Some authors have proposed ways to limit the migration of phthalates. Several techniques can be used such as covalent attachment of the plasticizer to the PVC chain [6], polyethylene oxide coating [7], chemical vapor deposition [8] and nucleophilic substitution of PVC with dithiocarbamate [9]. The recommended methods need to be optimized in order to improve the properties of the composite material.

Soft chemical synthesis conditions based on the hybrid sol gel route can provide a soft elaboration process required to coat a

fragile polymer substrate. In this work, we have developed an effective method to prevent the plasticizers release and UV degradation that involve covering the surface of the PVC with a thin organic/inorganic layer. We have synthesized an interpenetrating organic/inorganic network under mild condition. The inorganic skeleton is built by hydrolysis and condensation at room temperature, compatible with the presence of the organic moieties, whereas the polymer genesis is induced by a mild UV curing irradiation. The PVC substrate was coated using dip-coating process. The optical and structural properties of the coating were investigated by UV–visible and infrared spectroscopy. Further objectives of our investigation were two-fold. We measured the amount of phthalate that leached out from the hybrid coated PVC using HPLC. We evaluated the adhesion between the coating and the polymer substrate using a fragmentation test.

2. Experimental

2.1. Hybrid sol synthesis

The inorganic matrix precursor used was the methacryloxypropyltrimethoxysilane (MAPTMS) supplied by Sigma Aldrich. This organosilane has a photopolymerizable methacrylate function grafted on an alkoxy silane. In the first step of the sol synthesis, partial hydrolysis and condensation of the organoalkoxy silane was carried out under an acid catalysis condition by adding 0.75

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equ. molar of 0.1 M HCl with vigorous stirring [10]. Due to its high reactivity [11], the Sigma Aldrich titanium IV isopropoxide was first complexed with pure acrylic acid (AA) supplied by Sigma in the molar ratio $\text{Ti}(\text{O}^i\text{Pr})_4\text{:AA}$ 1:2 and then added to the pre hydrolysed medium. The inorganic molar ratio $\text{MAPTMS}:\text{Ti}(\text{O}^i\text{Pr})_4$ was 10:1. The second step was the hydrolysis and condensation of the previous mixture. Under a vigorous stirring, desionized water was dropped in order to reach the molar ratio $\text{H}_2\text{O}:\text{MAPTMS}$ 3:2 and $\text{H}_2\text{O}:\text{Ti}(\text{O}^i\text{Pr})_4$ 3:2. Under non actinic light, the photoinitiator in the form of 3 wt.% of Sigma Aldrich 2,2-dimethoxy-1,2-diphenylethane-1-one was added to the solution. The solution was stirred overnight and stored away from light. We obtained a hybrid sol with a composition 10:1:2 who stands for the molar ratio $\text{MAPTMS}:\text{Ti}(\text{O}^i\text{Pr})_4:\text{AcrylicAcid}$.

2.2. Samples coatings process

The films were dip coated on a PVC DEHP-plasticized substrate (6×1 cm) supplied by Macopharma and on a polished silicon wafer for the FTIR transmission measurements. The withdrawal speed is 25 cm/min. Just after the coating, the samples were irradiated for 20 min with a polychromatic fluorescent UV lamps (Philips TDL 8 W (total optical power, 1.3 W), 300 mm long, wavelength range 350–400 nm) in a configuration providing about 0.7 mW/cm² at the sample surface. During this UV curing process, an interpenetrating organic network is formed through a radical polymerization of the methacrylate and acrylate groups to produce a dense material [12]. PVC DEHP-plasticized substrate is sensitive to annealing treatment. So a soft UV curing condition is compatible with the PVC substrate. The curing treatment induces a photopolymerization process of the organic ligands. The syneresis liquid is replaced by the organic chains. This method led to the minimization of the volume shrinkage. The residual stress level does not induce a significant curvature on the coated PVC samples. We obtained a highly transparent coating without any cracking.

2.3. Transmission electron microscopy

The hybrid layer morphology was observed using a Hitachi transmission electron microscope (H-7650) with an 80 kV acceleration voltage. Micrographs were made using a Hamamatsu AMT numeric camera coupled with the microscope. To perform the characterization, a drop of the hybrid sol was deposited on a 300 mesh carbon-Formvar copper grid and dried at room temperature.

2.4. Optical and structural properties of the coating

The optical and structural properties were investigated using UV–visible and infrared spectroscopy. Transmission spectra of the samples coated on PVC were recorded from 200 to 900 nm with a resolution of 2 nm using a PerkinElmer Lambda 35 spectrometer. Infrared absorption spectra were acquired over the range 4000–400 cm⁻¹ with a PerkinElmer Spectrum Fourier transform infrared spectroscopy with a resolution of 2 cm⁻¹ on the thin films deposited on a polished silicon wafer.

2.5. Evaluation of plasticizers migration

The barrier effect of the above hybrid coating on the migration of DEHP was assessed by two methods: ATR-FTIR and DEHP migration test with chromatographic analysis of DEHP. 55 samples of PVC (6×1 cm) were used. These samples consist of untreated PVC or pretreated PVC with UV-ozone and plasma before the dip coating. The plasma and UV-ozone treatments could alter the interface properties of the PVC sample. The new state of the surface

may enhance the coating adhesion and act as an additional barrier against the phthalate release. The coated PVC samples were prepared by the above-described coating process. Samples were submitted to a sterilization process by plasma-based and/or UV-ozone treatments. The plasma low-temperature sterilization was performed with the STERAD 100 gas-plasma technique, employing hydrogen peroxide (58%). The sterilization cycle (duration 54 min) includes an hydrogen peroxide diffusion phase in the reactor (H_2O_2 was previously injected in the chamber under vacuum, maintained at 45°C) followed by a plasma phase (duration: 5 min) generated by an RF generator (13.56 MHz). During UV-ozone sterilization process, PVC substrates were subjected to a UV-ozone atmosphere at 30°C during 5 min. The sample method of DEHP migration evaluation is described in Table 1.

ATR-FTIR spectroscopy was performed using a PerkinElmer Paragon 1000 apparatus. The spectra were recorded using a single reflection diamond crystal, co-adding 40 scans. The 1426 cm⁻¹ and 1463 cm⁻¹ bands were used as the reference bands for the polymer and the plasticizer, respectively. The ratio absorbance_{1463 cm⁻¹}/absorbance_{1426 cm⁻¹} allows the evaluation of the amount of plasticizers present on the surface of the PVC DEHP-plasticized substrate. A PVC containing 34% of DEHP was used as a standard for the calculation (absorbance_{1463 cm⁻¹}/absorbance_{1426 cm⁻¹} = 1.075).

The sample method of DEHP migration evaluation is described in table 1. For the DEHP migration test, each sample was soaked into a 30 mL solution of ethanol 96% (Sigma Aldrich) during one hour at room temperature. Ethanol was chosen in order to respect the conditions of migration described in the European Standard EN 1186-15 [13]. After homogenization, 1 mL of the solution was removed in order to measure the DEHP concentration by HPLC. The utensils and the solvents used for migration tests are free of DEHP. The glass-work was systematically washed with methanol and tetrahydrofuran before use. Chromatographic analysis was performed using a LC-2010C integrated high performance liquid chromatographic system (Shimadzu). The separation was achieved using a 5 μm Lichrospher 100 RP 18 endcapped column (125 × 4.6 mm ID) (Macherey-Nagel). The mobile phase consisted of a mixture of acetonitrile, tetrahydrofuran and water (70:15:15 v/v), at a flow rate of 1.5 mL/min. The detection wavelength was set up at 254 nm. The injection volume was 50 μL. The DEHP presents a retention time of 5.6 min. This chromatographic method is linear for concentrations ranging from 5 to 200 μg/mL. The mean linear regression equation obtained is $y = 8132.1x + 5193.4$ ($r^2 = 0.9999$), where x is the DEHP concentration and y the surface area of the corresponding peak. This method has acceptable accuracy and precision with the intra-assay and inter-assay coefficients of variation all below 5.5%. The detection threshold was 2 ppm.

2.6. Mechanical and adhesion studies

Several techniques are used to study the mechanical properties of polymers such as scratch resistance test [14]. The mechanical characteristics of PVC and coated PVC have been determined using a tensile test. The tests were carried out on 60×10 mm² sample strips, with a strain rate maintained at $4 \cdot 10^{-4}$ s⁻¹. The mechanical properties of the coating have been assessed from the stress–strain curve of the hybrid film, obtained by separating the force working on the polymer from that working on the coated polymer sample [15–18]. The adhesion between the coating and the polymer substrate was analysed in terms of the interfacial shear strength. The test developed in this study is the tensile shear test also called fragmentation test, currently used as an adhesion testing method for brittle films on ductile substrates [19–23]. The theory of this test [24] is relevant to describe the interfacial stress transfer from the substrate to the coating. In this adhesion testing technique, the

Table 1
Sample method of DEHP migration evaluation.

Batch name	Description	Number of samples		Treatment		
		ATR-FTIR	Migration test	Plasma	Ozone	Sol-Gel
C	Controls	1	6	None	None	None
P	Plasma	1	6	X	None	None
O	UV-Ozone	1	6	None	X	None
HSG	Hybrid sol gel	1	6	None	None	X
P-O	Plasma +UV-Ozone	1	6	X	X	None
P-HSG	Plasma +Hybrid sol gel	1	6	X	None	X
O-HSG	UV-Ozone +Hybrid sol gel	1	6	None	X	X
P-O-HSG	Plasma +UV-Ozone +Hybrid sol gel	1	6	X	X	X

coating-substrate system is loaded under uniaxial tension and the fragmentation state in the coating is studied as a function of strain. Based on this approach, the interfacial shear strength, τ , is obtained by the following stress transfer equation [25]:

$$\tau = \frac{2h_c\sigma_{\max}}{l_c} \quad (1)$$

Where h_c is the coating thickness, σ_{\max} is the coating tensile strength, and l_c is the critical stress transfer length (the minimum coating length in which the maximum coating stress σ_{\max} is achieved). The critical length l_c is related to the average fragment length at saturation (state obtained when an increase in strain does not lead to further fragmentation in the coating) [26]: $l_{\text{sat}} = 0.67 l_c$.

3. Results and discussion

3.1. Hybrid sol synthesis

The hybrid sol is a mixture of two organic modified alkoxides [27]. The main component is the methacryloxy propyl grafted silicon alkoxide. The first step of our process is the slow hydrolysis of this precursor in order to build the first covalent links between the silicon species and it gives rise to the so called silicon sol described in Fig. 1. Simultaneously, the titanium IV isopropoxide is chelated with acrylic acid in order to decrease its reactivity toward the hydrolysis process, we obtain the titanium complex solution. Then, the two parts are mixed together and a cohydrolysis is carried out in order to establish the first entities of the further silica backbone with some inclusions of titanium clusters. We obtain a hybrid sol. The last part of the synthesis is the addition of

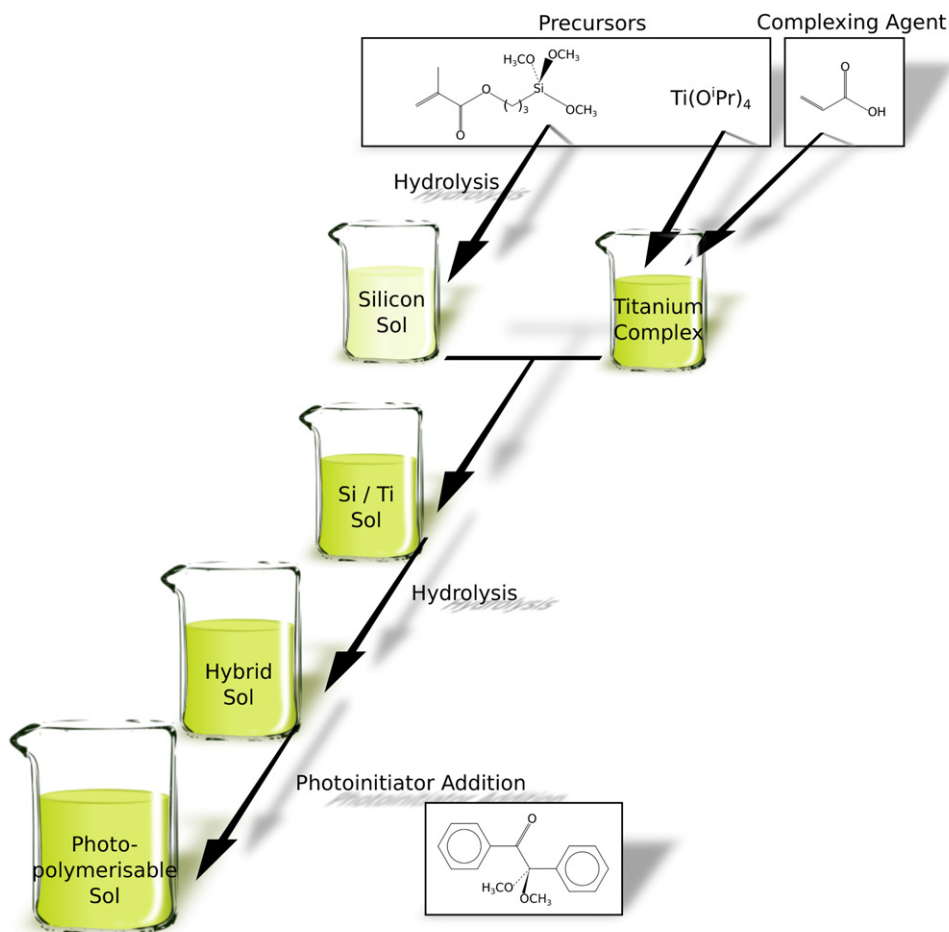


Fig. 1. Schematic of the main steps of the photopolymerisable sol synthesis hybrid containment layer synthesis.

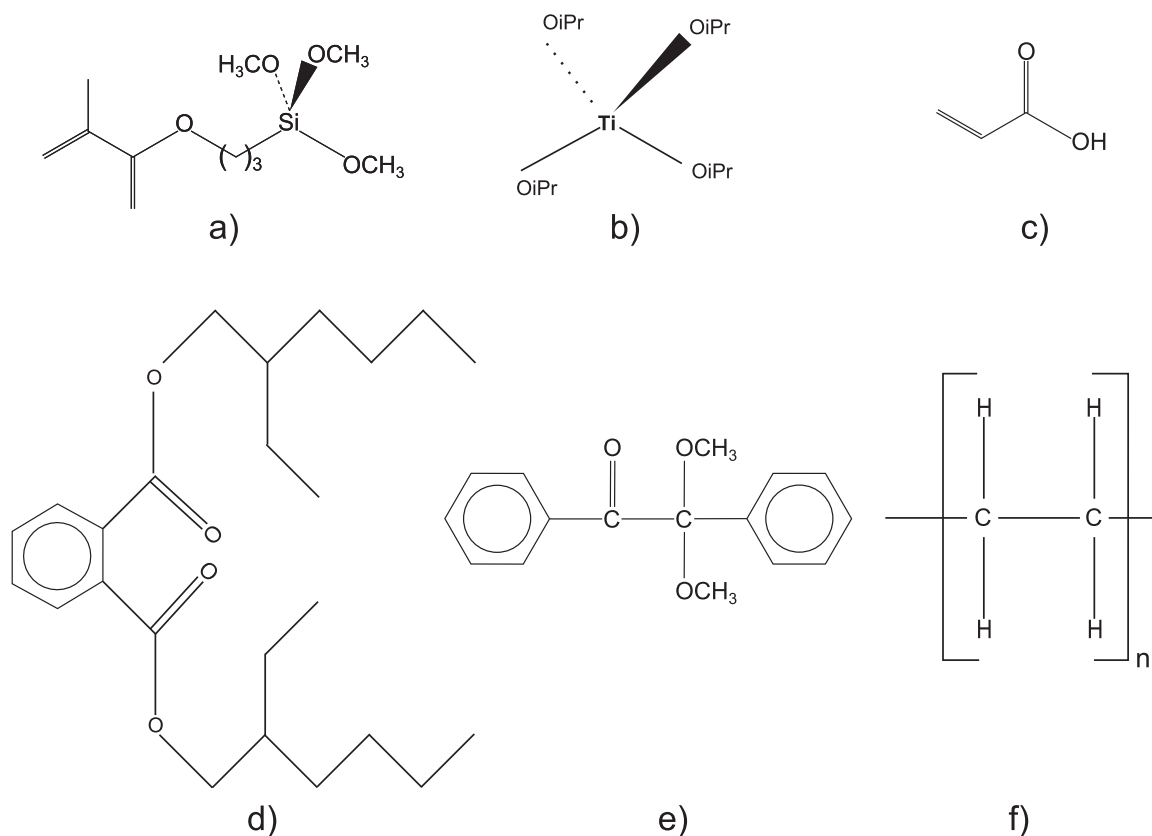


Fig. 2. Chemical structures of the various chemical components used (a) methacryloxypropyltrimethoxysilane (b) titanium IV isopropoxide (c) acrylic acid (d) Di(2-ethylhexyl) phthalate (DEHP) (e) 2,2-dimethoxy-1,2-diphenylethan-1-one (f) polyvinyl chloride.

the photoinitiator 2,2-dimethoxy-1,2-diphenylethan-1-one under non actinic light to form the photopolymerisable hybrid sol.

The deposition onto the polymer substrate was achieved by dip coating. Chemical structures of various chemical components used are shown in Fig. 2. The class II hybrid thin films are tunable materials in which the organic and inorganic parts are linked at molecular scale by covalent bonding that remain stable in the synthesis conditions [28]. By this way, a thin homogeneous composite film that combines the advantages of the polymer (suppleness, versatility) and some physical properties of a glass (mechanical resistance, transparency) is elaborated.

In order to finalize the layer's properties, a reactive drying process is then induced by a photopolymerization step to develop the organic crosslinking between the different polymer moieties

grafted on the inorganic clusters. The process is shown Fig. 3. Under UV irradiation, the photoinitiator molecular species are decomposed and free radical species initiate the polymerization process of the vinyl groups [29]. We obtain a hybrid film with an organic matrix linked to the inorganic skeleton at the molecular scale. This kind of versatile nanocomposite material is a very interesting candidate to form high efficiency containment layer.

Fig. 4 shows the absorbance spectra of the hybrid film coated on PVC substrate compared with the absorbance of the naked PVC substrate (air was taken as a reference while acquiring the data). As far as the uncoated PVC substrate is concerned, the absorbance is very high in the 200–300 nm range. The coated sample has difference absorbance spectra, in the UV-C range; the coating has an effect with the appearance of the sharp peaks. The main result is that the

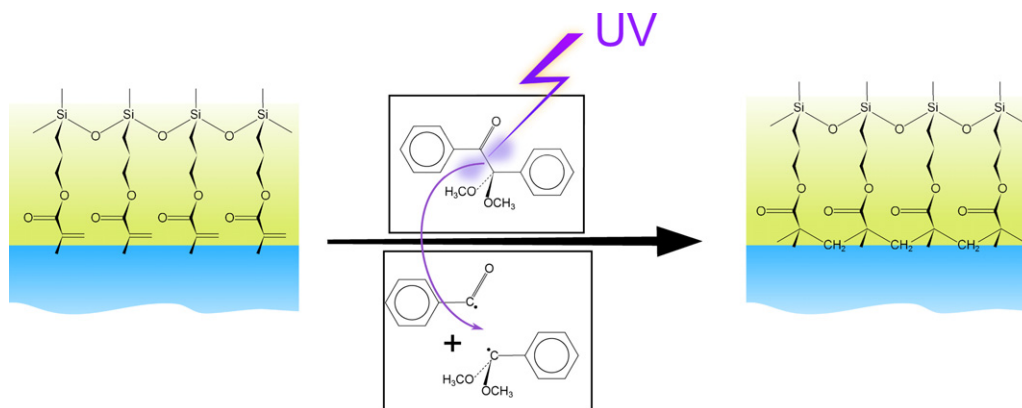


Fig. 3. Schematic of the UV induced photopolymerization process.

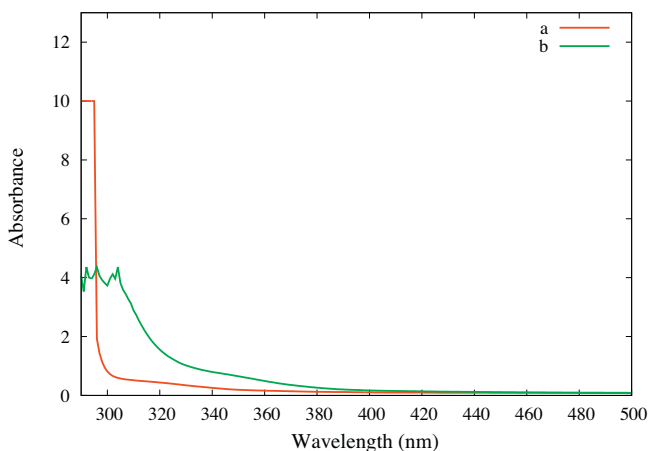


Fig. 4. UV absorbance spectrum of the uncoated PVC (a) given as reference. UV absorbance spectrum of UV cured hybrid film on the PVC substrate (b).

coating has a fair UV-A filter effect in the 300–400 nm range. So the coating can prevent the UV induced degradation of the polymer material.

3.2. Transmission electron microscopy

Transmission electron microscopy (TEM) images were obtained from a diluted solution of the hybrid sol. A typical image is shown in Fig. 5. The dark areas of the picture seem to indicate the presence of inorganic particles because they scatter electron far more efficiently than the organic component. The lighter portion of the image is likely to be the organic polymer component. The composite hybrid layer seems to present inorganic clusters embedded in polymeric matrix.

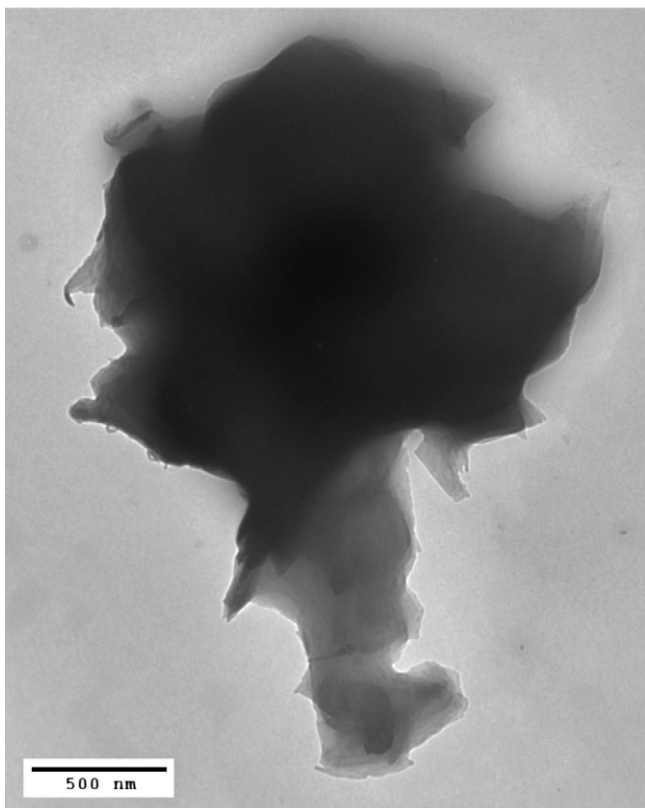


Fig. 5. TEM image of the hybrid coating.

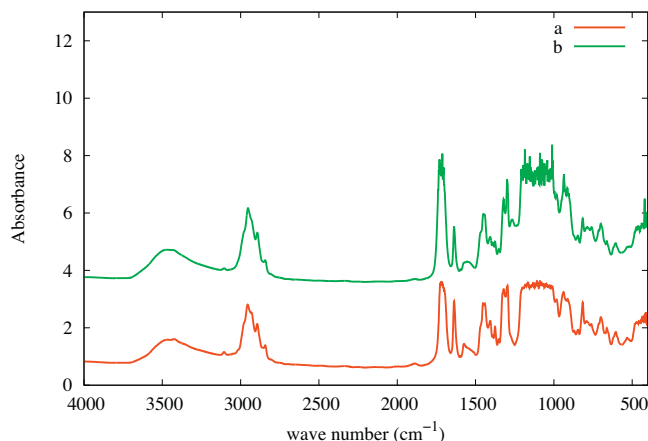


Fig. 6. FTIR spectra of a film of composition 10:1:2 before UV curing (a) and after 20 min of UV curing (b). Spectra are offset for a better viewing.

3.3. Infrared spectroscopy

Infrared spectroscopy was used to follow the inorganic network formation through the hydrolysis and condensation reactions and the development of the organic network during the UV curing. Fig. 6 shows the full range spectra of a film of composition 10:1:2 recorded just after deposition and after 20 min of UV curing. First, at high wavenumbers, the bands associated with OH (around 3440 cm⁻¹), CH (2947 cm⁻¹) and CH₃ (2887 cm⁻¹) are observed. An inorganic backbone signature is presented mainly in the 900–1230 cm⁻¹ range of the spectra. The broad band between 1000 and 1200 cm⁻¹ is attributed to the Si–O–Si bonds. In the UV treated sample spectrum, some broadening of the Si–O–Si starts to appear, in these hybrid coatings, the polymerization of the organic moieties induces collateral structure change of the silica network. Concerning the organic polymerization, it can be underlined in the mid IR region by the decrease of the intensity of the vinyl group C=C at 1635 cm⁻¹. The photo induced radical polymerization can be followed by the disappearance of the acrylate groups. The radical polymerization converts the C=C double bonds into C–C single bond. The conversion ratio is defined as the residual amount of C=C double bonds at a given UV curing time over the initial amount of the C=C double bonds before the irradiation:

$$C(t) = \left(1 - \frac{A_t(\text{C}=\text{C})}{A_{t=0}(\text{C}=\text{C})} \right) \times 100 \quad (2)$$

where $A_t(\text{C}=\text{C})$ and $A_{t=0}(\text{C}=\text{C})$ are the area of the C=C band at $t=0$ and t respectively [30].

In our case after 20 min of UV curing, we recorded the spectra shown in Fig. 7. We measured the conversion ratio $C(t) = 30\%$ after 20 min of the UV curing by comparison between the areas under the curves. This value is well suited for the coating of the plasticized PVC as it leads to an efficient containment layer with the requested suppleness [31–33].

3.4. DEHP migration test

Fig. 8 summarizes the DEHP release studies from both untreated and treated PVC coated or uncoated with the sol gel layer. The measurements were achieved using HPLC. After a one hour contact, DEHP is released from control samples (C) and the mean concentration obtained in ethanol is 207.3 ± 35.4 g/mL. It is clearly demonstrated that plasma and UV-ozone curing have a negligible effect on the DEHP migration reducing it only by 10–12% (column P and O). Even if they are both combined on the PVC surface, DEHP leaching is high. The coated PVC samples are resistant to DEHP

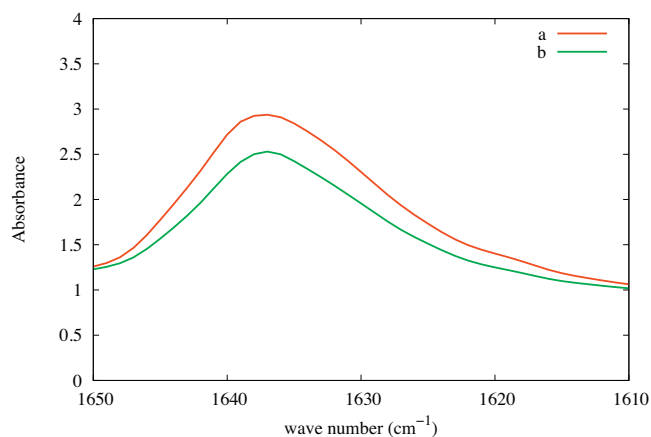


Fig. 7. Area decrease of C=C band at 1635 cm^{-1} recorded from FTIR spectra: (a) before UV curing (b) after 20 min of UV curing.

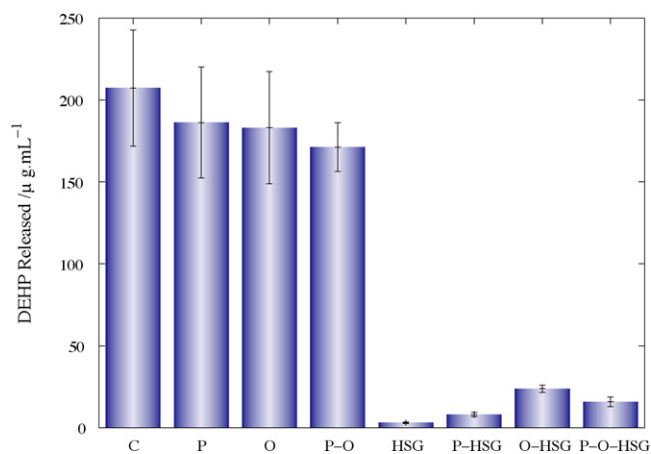


Fig. 8. Impact of different PVC surface treatments on DEHP migration into ethanol solution.

migration and the protection from leaching is 98.5%, compared to the controls. When the coating is combined with plasma or ozone, DEHP migration is also reduced. But a pre-treatment by plasma or ozone or both doesn't improve the protection from DEHP leaching. Leaching is only reduced to 88.5% and 93.8%, respectively.

3.5. ATR-FTIR

The different samples analysed by ATR-FTIR are shown in Table 2. The samples are hybrid coated PVC substrates with different pretreatment on the polymer substrates.

FTIR spectra of Fig. 9 clearly indicate that the plasticizer is no more detected on the surface of the coated PVC. The effect of the coating on DEHP migration is efficient. This is consistent with the DEHP migration test results which indicated an excellent resistance of the coated PVC to DEHP migration.

We also conclude that the surface treatments by plasma or UV/ozone have no effect on the prevention of plasticizer migration

Table 2
Evaluation of DEHP ratio on PVC surface by ATR-FTIR spectroscopy.

Treatment	Absorbance $^{-1}_{1463\text{cm}^{-1}}$ /Absorbance $^{-1}_{1426\text{cm}^{-1}}$	DEHP ration (%)
untreated	0.883 ± 0.009	27.9 ± 0.3
plasma	0.902 ± 0.021	28.5 ± 0.6
UV/ozone	0.916 ± 0.004	29.0 ± 0.7
plasma +UV/ozone	0.904 ± 0.019	28.6 ± 0.6

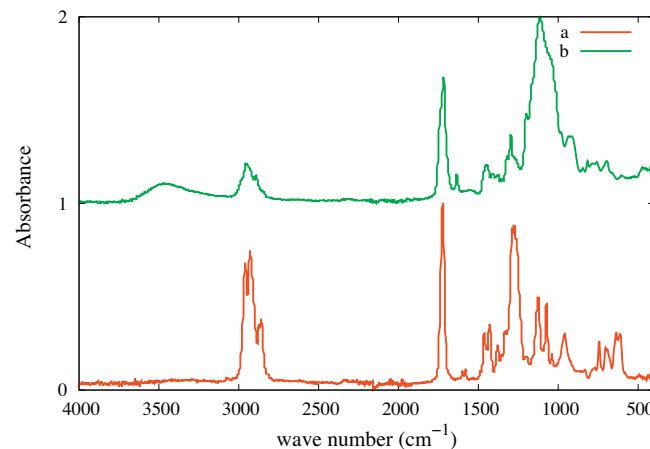


Fig. 9. ATR-FTIR spectra of naked PVC (a) and coated-PVC (b).

since the DEHP ratios measured are nearly equivalent and do not differ from the ratio obtained with the untreated PVC. This result also confirms the assertions deduced from the DEHP migration test. One can also note that the polymer substrate cannot be identified on the coated PVC IR spectrum. The action of plasma results in crosslinking, functionalization and chain scission (etching), the relative importance of each phenomenon depending on the plasma conditions and the polymer. Crosslinking was expected to prevent the migration of additives. Crosslinking can result from exposure to plasma treatment of inert gases such as argon plasma [34], but can also be surmised to explain plasticizer migration decrease in PVC DEHP-plasticized substrate submitted to UV irradiation [35]. In the present study, the treatments applied do probably not induce significant crosslinking on the polymer surface, given the test conditions used, developed for sterilization process.

3.6. Tensile tests

The results in Table 3 indicate, in the first hand, that the surface treatment by plasma or UV/ozone has no significant effect on the mechanical properties of the polymer. On the second hand, it is obvious that these properties are drastically altered when the surface of PVC is covered by the hybrid film.

The thicknesses of the polymer and of the hybrid coating were measured respectively at 300 microns and 50 microns, with some minor variations around these values (which have been taken into account for calculation). The hybrid layer exhibits a stiffer and less ductile behaviour than the polymer. The Young's modulus of the hybrid coating reaches $1.48 \pm 0.08\text{ GPa}$. This latter value is approximately 50 times higher than that obtained for the polymer. The hybrid film/PVC assembly breaks at an elongation rate which was about 7 times lower than that measured for PVC; a mean value of

Table 3
Evolution of mechanical properties of PVC and coating/PVC assembly consecutive to surface treatments.

Surface treatment	Young's modulus (MPa)	Elongation at break (%)
untreated	33.1 ± 2.1	443.9 ± 96.5
plasma	31.4 ± 3.0	406.3 ± 127.5
UV/ozone	31.1 ± 5.2	386.7 ± 145.3
plasma +UV/ozone	28.9 ± 4.7	370.8 ± 180.4
coating	285.7 ± 11.9	53.4 ± 4.0
plasma +coating	282.1 ± 27.3	56.8 ± 5.7
UV/ozone +coating	311.6 ± 50.2	49.3 ± 17.8
plasma +UV/ozone +coating	294.7 ± 104.7	73.1 ± 14.5

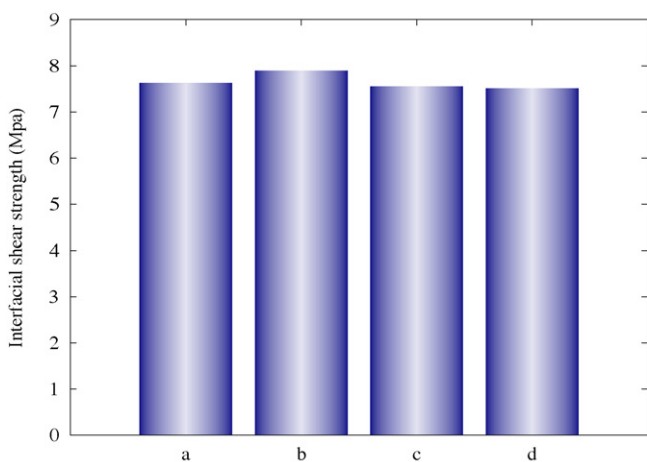


Fig. 10. Evolution of interfacial shear strength versus polymer surface treatments: (a) untreated, (b) plasma, (c) UV/ozone, (d) UV/ozone + plasma.

$58.2 \pm 16.6\%$ is obtained for the elongation at break of the coated PVC.

3.7. Adhesion behavior

The coating tensile strength σ_{\max} , deduced from the stress-strain curves was found to be constant for all specimens (contained between 21.2 and 22.2 MPa), with a mean value of 21.5 ± 0.7 MPa. The measurements of the average fragment length at saturation \bar{l}_{sat} , allow calculation of the interfacial shear strength from Eq. 1. The data of τ , reported in Fig. 10, indicate that the adhesion of the hybrid film on the polymer is not significantly altered by the treatment performed on the PVC surface. The values of τ range over a slight field around 7.64 ± 0.27 MPa.

4. Conclusion

In this work, we demonstrate the efficiency of a photopolymerisable hybrid sol gel coating against the plasticizer's release. The layer exhibits a high containment effect, providing by the fact that our film is a nanocomposite made by two highly interpenetrated matrixes covalently bounded together. We have successfully fabricated an organic/inorganic hybrid layer on a polymer substrate, generated by the hydrolysis and condensation of a mixture of a titanium alkoxide functionalized by an acrylic acid and a methacrylate grafted alkoxy silane. The hybrid layer exhibits a stiffer and less ductile behavior than the polymer. The surface treatment of the polymer does not alter the adhesion of the hybrid coating on the polymer. The migration tests performed show very interesting results. The layer is efficient in stopping the plasticizers' release; the plasticizers are no more detected on the surface of the coated PVC. The coating also provides high transparency to the coated material and acts as a UV filter that prevents the UV induced degradation of the polymer. The use of a highly tunable hybrid layer paves the way to further investigations in order to optimize the requested properties of the containment barrier. The organic/inorganic ratio, the crosslinking level between these two parts, and the coating thickness are promising parameters in order to tailor the film properties.

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