ALJEST

Study of methods to reduce contamination of food from food packaging based on plasticized PVC (argon plasma)

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ARTICLE INFO	ABSTRACT/RESUME
	Abstract : In this work we studied a surface treatment process using argon plasma to reduce the migration of the additives contained in the initial plastic package (PVC) stabilized with sunflower oil epoxidized and to identify the migrant substances. *One formulation was considered (in the presence of 40 % of plasticizer), migration tests are done under 40°C with agitation in crude olive oil.* *The migration phenomenon is studied on the bases of a preliminary analysis on the variation of the weight of test tubes of PVC with the help of three technical analyses: Fourier transform infrared (FTIR) and scanning electron microscopy (SEM).*

1. Introduction

Material in contact with food must ensure its protection and conservation, without altering its organoleptic or physicochemical: it is the principle of inertia [1-3]. Now we also know that contacting a plastic container with food induces unavoidable contamination of the food and can lead to interference and may give unknown compounds called neo formed or send her a taste and an unwanted odor or changes in the properties of the plastic material which will become unable to protect optimally the food [4]. In order to reduce this mechanism, different approaches have been developed:
1. Surface modification;
a. Crosslinking surface;
b. Changing the surface: hydrophilic / lipophilic;
c. Siding
d. Extraction surface;
2. Permanent use of plasticizers;
3. Combination of the two above-mentioned;

We tried to reduce this migration by modifying the polymer surface by crosslinking using a cold plasma source with argon as the plasma gas.
This method aims to approximate the molecular chains of the polymer thus increasing cohesion and decreasing the free volume and create a three-dimensional network which will act as a barrier and additives contained in the package to migrate to the food and the same time, the food from entering the interior of the polymer.
The cold plasma treatment depends on four important parameters:
- The power of plasma;
- The exposure time of the plasma samples;
- The pressure inside the plasma reactor;
- The distance between the source and the sample.
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II. Materials and methods

The phenomenon of migration is analyzed and based on the change in mass of PVC pellets in contact with the environment simulator as well as using the Fourier transform infrared (FTIR), further characterization of the morphology of the pellets was carried out by scanning electron microscopy (SEM).

II.1. Preparation of PVC films

Resin and additives, whose proportions are specified in Table 1 were mixed in methanol [5], which is then removed by evaporation in an oven at 60 °C.
The mixture obtained is perfectly homogeneous then introduced into a mixer with two rotary cylinders, heated at 135 °C for 15 to 20 minutes. The gelled mixture is then placed between two plates (Table press Fontijne) at 170 ° C under a

pressure of 300 KN for 5 minutes to obtain the desired thickness (2.0 ± 0.1) mm.

Table 1. Formulation of PVC films

Formulation	Weight (%)
PVC resin	100
Zn and Ca stearates complex	2
Stearine	1
Epoxidized sunflower oil (ESO)	10
Di-octyl-phtalate (DOP)	40

II.2. Argon plasma treatment

The device is composed of experimental:
- A spherical enclosure stainless steel 1m in diameter. It is connected to a pumping system (primary and secondary) for discharging air to achieve a vacuum of the order of 10^{-6} mbar.
- An inductive source. The power control is done by a RF radio frequency generator (13.56 MHz) via impedance.

In our study, we followed three parameters of power, pressure and time of exposure; the distance was set at 1 cm from the source. To this end, we conducted a sweep of power between 60 and 120W, exposure times ranging from 1 to 3 minutes and the pressure $7,5.10^{-2}$ mbar, $1,0.10^{-1}$mbar and $1,1.10^{-1}$ mbar (Table 2).

Table 2. Working conditions of Argon Plasma Reactor

Indice	Conditions
CN 1 a	P= 120W, t= 3mn, D= 20sccm, d= 1cm, p= $7,5.10^{-2}$mbar
CN 1 b	P= 120W, t= 1mn, D= 20sccm, d= 1cm, p= $7,5.10^{-2}$mbar
CN 2 a	P= 100W, t= 3mn, D= 20sccm, d= 1cm, p= $7,5.10^{-2}$mbar
CN 2 b	P= 100W, t= 1mn, D= 20sccm, d= 1cm, p= $7,5.10^{-2}$mbar
CN 3 a	P= 80W, t= 5mn, D= 20sccm, d= 1cm, p= $7,5.10^{-2}$mbar
CN 3 b	P= 80W, t= 3mn, D= 20sccm, d = 1cm, p= $7,5.10^{-2}$mbar
CN 3 c	P= 80W, t= 1mn, D= 20sccm, d = 1cm, p= $7,5.10^{-2}$mbar
CN 3 d	P= 80W, t= 2mn, D= 30sccm, d = 1cm, p= $1,0.10^{-1}$mbar
CN 3 e	P= 80W, t= 2mn, D= 40sccm, d = 1cm, p= $1,1.10^{-1}$mbar
CN 4 a	P= 60W, t= 3mn, D= 20sccm, d = 1cm, p= $7,5.10^{-2}$mbar
CN 4 b	P= 60W, t= 1mn, D= 20sccm, d = 1cm, p= $7,5.10^{-2}$mbar

II.3. Test migration

The kinetics were followed by isothermal for10 days at 40°C in 50 ml of liquid simulator controlled agitation continues. A sample is taken every 48 hours (PVC disc10 mL crude olive oil) to keep the ratio (oil volume) / (number of disks) [6].

To identify the nature of the phenomenon occurring during contact with PVC pellets mid simulator foods (raw olive oil) and know the overall migration rate, the evolution of the change rate of

pellets mass depending on the contact time in hours was followed with [7]:

$$\tau(\%) = \frac{m_t - m_0}{m_0} \times 100$$

Where: m_t: mass of the pellet collected on day dafter wiping, still weigh in guntil the weight becomes constant (about 5 or 6 days).

m_0: mass of the pellet before initial immersion in the simulator.

The decrease of the ratio means the passage of a certain quantity of the additive polymer in the middle simulator and conversely increases the penetration means of the simulator environment in the specimen [8].

II.4. FTIR spectroscopy analysis

The PVC samples were dissolved in tetrahydrofuran. After evaporation of the solvent, a polymeric film was recovered and analyzed with a Jasco FTIR- 430 spectrophotometer. The resolution was 2 cm^{-1}.

II.5. SEM characterization

The PVC samples were analyses after metallization by a scanning electron microscopePHILIPS type ESEM XL.

III. Results and discussions

III.1. Migration testin

We notice that in general, the curves are decreasing, and this in dictates a decrease in the rate of change of mass as a function of time and therefore a migration of certain additives took place. In addition, the kinetics of decrease is much more marked in the case of the untreated plastic formulation compared to that which has been processed. This shows that the argon plasma treatment of the latter decreased the migration.

DOP plasticizer incorporated into the polymer partially destroyed the interactions between PVC chains are responsible for the cohesion of the material and helps to change the properties of PVC. Cohesion reduced and the existence of a concentration gradient induced diffusion of additives in PVC pellet (concentrated medium) mid simulator.

We note from Figures1 and 2bothpower and pressure settings have a positive effect on the reduction of the phenomenon of migration quite large in comparison with the untreated material. In addition, although the difference is not significant, the pellets that were treated for 3min have been the least transfer phenomenon that those who were treated for 1min..
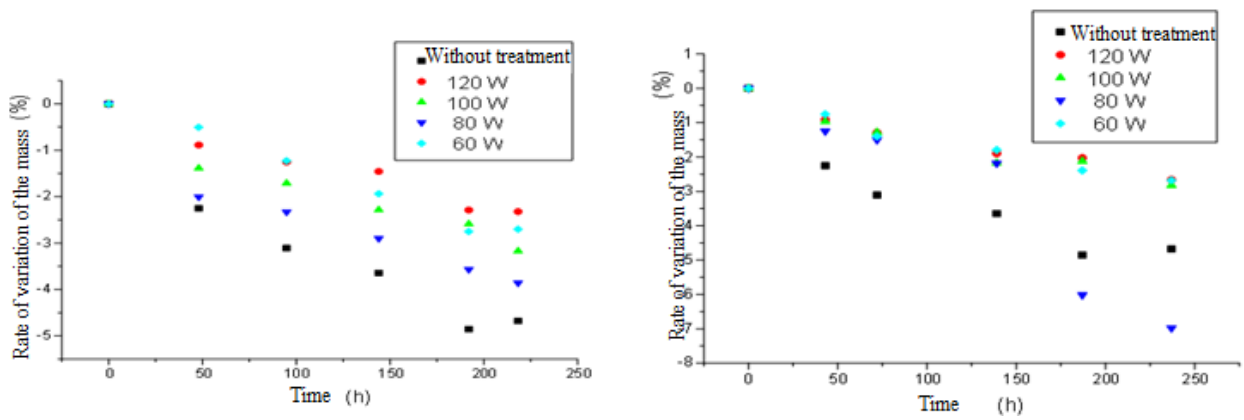
Figure 1. *Effect of power on the rate of change of mass for a fixed pressure7, 5.10⁻²mbarand a fixed exposure time: A-3min, B-1min*
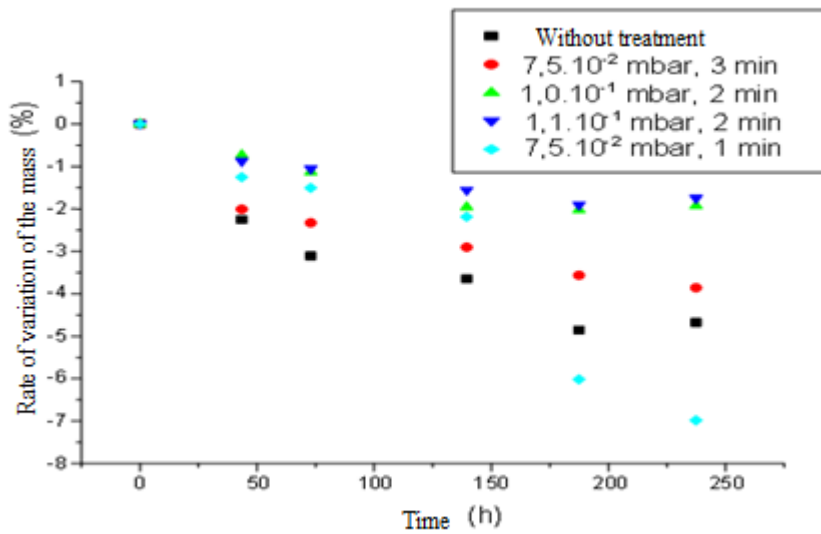

Figure 2. *Effect of pressure on the rate of change of mass power set at 80Wandan exposure time set to 2min*
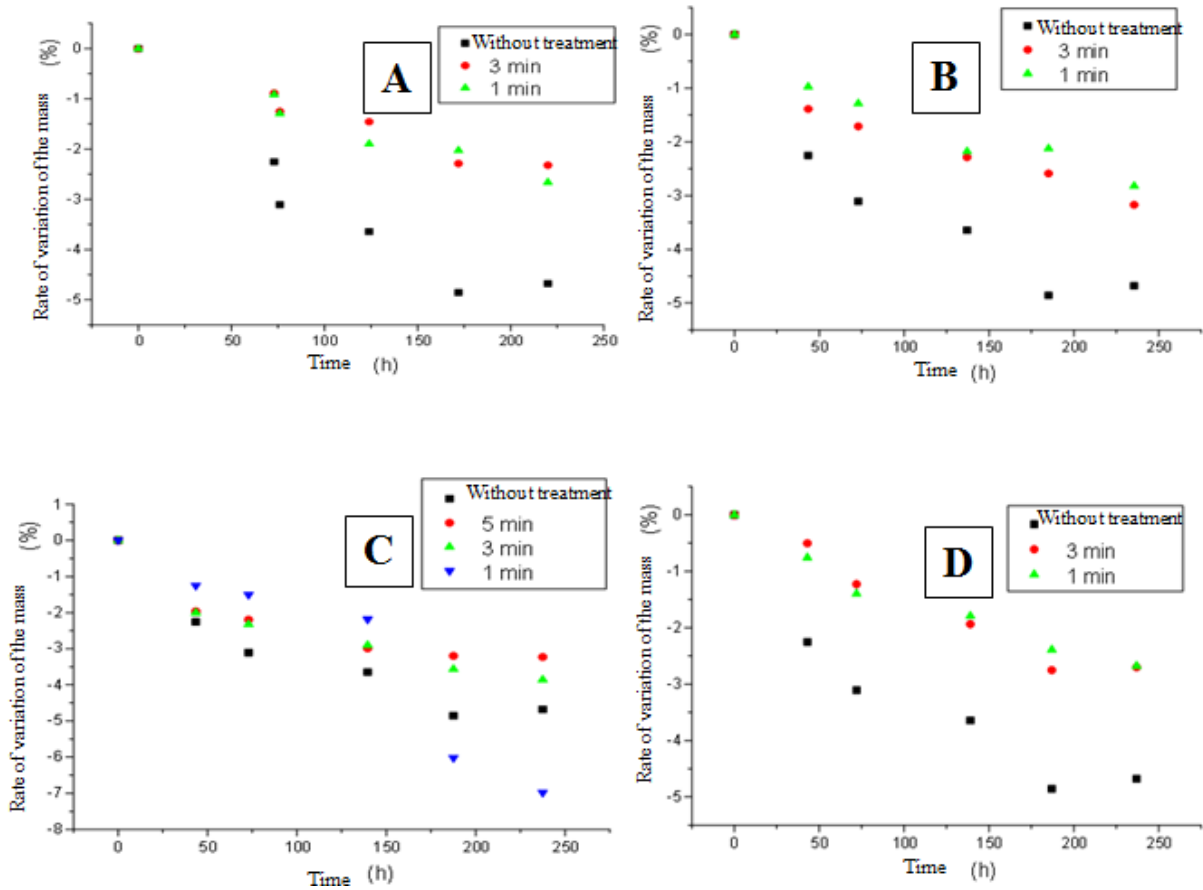
Figure 3. *Effect of exposure time on the rate of change of mass in a fixed pressure 7,5.10^{-2} mbar and a power set at: A-120W, B- 100 W, C-80 W, D- 60 W.*

Therefore, the greater the pressure is, the more we will charge species inside the reactor; and thus the probability that these species collide with the material increases. In the same spirit, the greater the power is, the greater the intensity of UV radiation and visible increase and charged species will have a greater speed, and the clash between the reactive species and the polymer surface will be greater.

All values of global migration plans are lower overall migration established by the EEC for plastic packaging is 10mg.dm^{-2}, which means that the migration did not affect the quality of the environment simulator (food) used.

In addition, the values of smaller global migrations are obtained in the case of Argon plasma treated pellets, confirming the effectiveness of this approach in reducing the overall migration of additives. In addition, there was a decrease in overall migration of more than 50% for the treated pellets under the conditions CNCN3d and 3e for which we had changed pressure.

Conditions						
	With traitement	CN1a	CN1b	CN2a	CN2b	CN4a	CN4b
Overall migration (mg.dm^{-2})	4,94	2,91	2,95	3,38	3,02	2,29	2,78

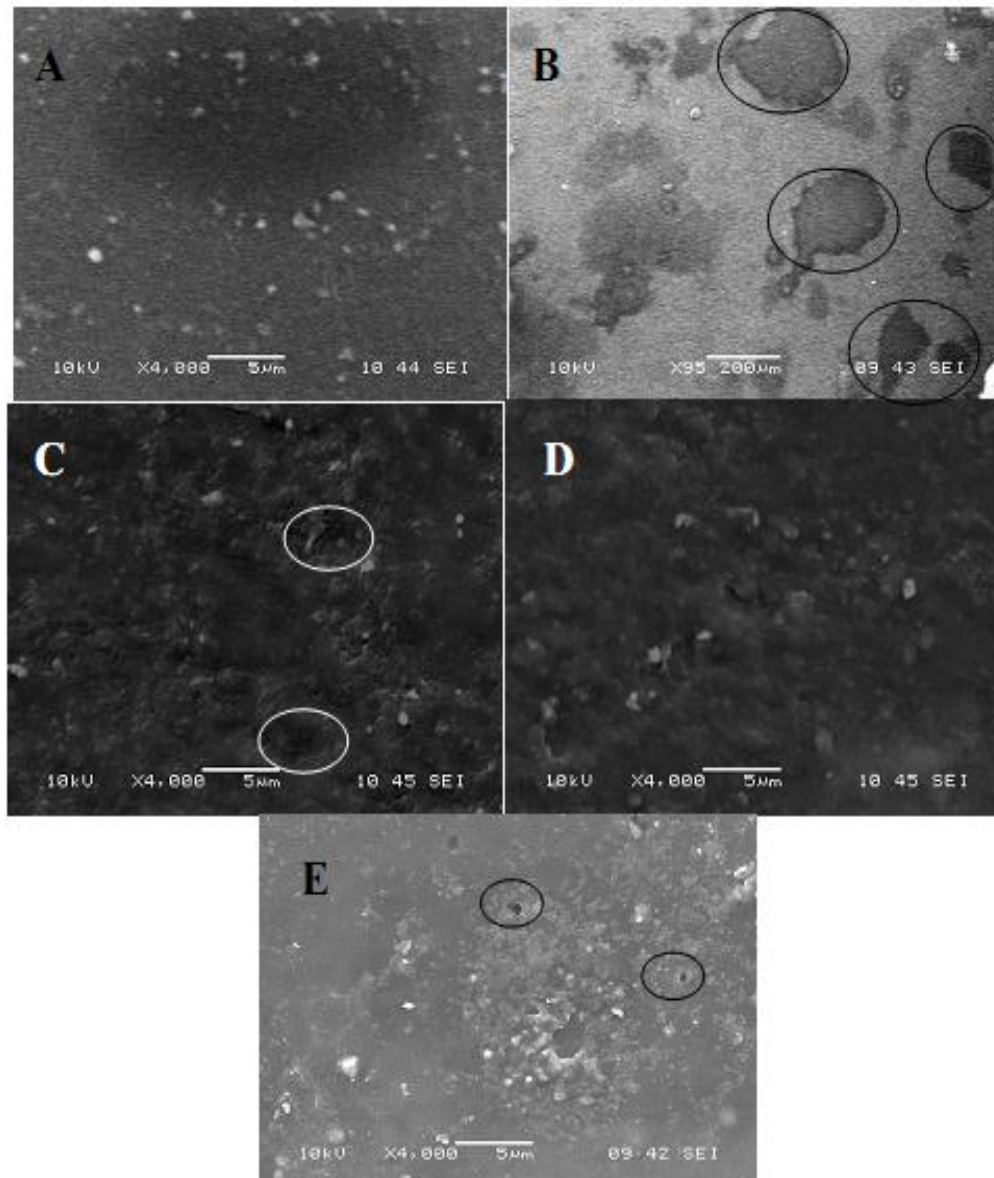| Conditions					
	With out traitement	CN3a	CN3b	CN3c	CN3d	CN3e
Overall migration (mg.dm^{-2})	4,94	2,26	4,13	5,44	2,12	1,83

III.2. SEM morphological analysis

Figure 4. *SEM analysis PVC pellets*
A- pellet-witness, witness after pellet B-10j contact with HOB,
C-treated wafer (under the conditions CN 1a) after contact with 10j HOB
D-treated wafer (under the conditions CN 2a) after contact with 10j HOB
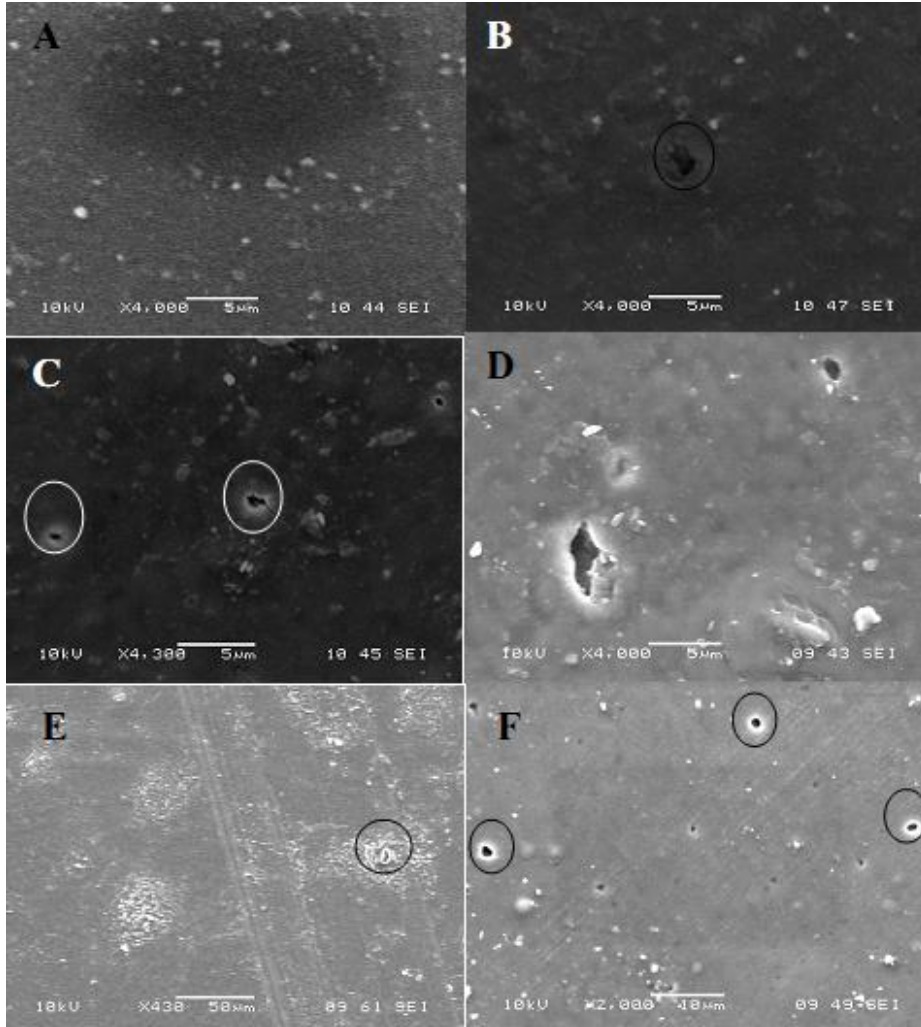*E-processed wafer (under the conditions CN 2b) after contact with 10j HOB*

***Figure 5**. SEM analysis PVC pellets*
A- pellet-witness
B-treated wafer (under the conditions CN 3a) after contact with 10j HOB
C-treated wafer (under the conditions CN 3b) after contact with 10j HOB
D-treated wafer (under the conditions CN 3c) after 10 h of contact with the HOB
E-treated wafer (under the conditions CN 4a) after contact with 10j HOB
F-treated wafer (under the conditions CN 4b) after 10 h of contact with the HOB.

By comparing the images of the controlled sample and those having under gone migration testing for 10 days, we observe:
- The appearance of dark are as (holes) indicating that there was migration of additives mid simulator;
-The surfaces of the pellets which have under gone migration tests are rough in comparison with the control, which has smoother surfaces;
- Holes observed are more important in the case of PVC untreated samples;
-The PVC pellets treated with argon plasma have less dark are as indicating that the treatment was effective.

III.3. Infrared spectroscopic analysis
In the presence of a mixture of polymer and additives, the spectrum represents the total sum of the spectra of the individual components. The interpretation is done by comparison with reference spectra of the known products based on tape, however, may have characteristics of the sample to be studied [8].

The band at 1432 cm^{-1} present in the spectra of the studied formulation as well as the PVC resin is the CH_2 bond in PVC [8]. It is taken as a reference for the calculation of the ratios of the absorbance for semi-quantitative estimation of the migration of additives.

A1725 /A1432: Study of the migration of DOP and HTE.

A1577 /A1432: Study of the migration of the complex Ca, Zn.

A 1460/ A1432: Study of the migration of DOP, the complex Ca, Zn and stearic acid.

A1121 /A1432: Study of the migration of DOP.

Overall, we note that the absorbance ratios are lower in the case of argon plasma treated pellets than those who were, indicating that migration is more important for them. The crosslinking argon plasma increases benefit cohesion with in the PVC molecule, and therefore the migration of additives is less important. We see also that in the case of almost all curves in FiguresVII.7.to VII.10., Reports absorbance increased up to48 hours, then gradually decreased. This case has already been observed in other studies [9]. It indicates an initial penetration of the liquid in the calculator PVC tubes, which has the effect of causing or enabling the migration of the present additives.

IV. Conclusion

In conclusion, the surface treatment to destroy the main routes connecting the chlorine in carbon chains of PVC, has helped bringing the molecular chains of the latter increasing the cohesion between the chains thus reducing the free volume and create A three-dimensional network which will act as a barrier to the transfer phenomenon. This barrier will be unfavorable to diffusion and therefore result in a decrease in migration. The plasma consists of atoms and molecules in the excited state and emits more charged species such as ions and electrons; radiation is visible to the naked eye. These reactive species of the plasma induced radical formation on the surface of PVC, which can lead to cuts in chains, to transfer reactions or recombination leading to crosslinking; i.e.: formation of a three-dimensional network of the polymer surface

V. Références bibliographiques

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