Cold Plasma Surface Modification of Conventionally and Nonconventionally Plasticized Poly(vinyl chloride)-Based Flexible Films: Global and Specific Migration of Additives into Isooctane

J.-L. AUDIC, F. PONCIN-EPAILLARD, D. REYX, J.-C. BROSSE

Laboratoire de Chimie Organique Macromoléculaire, UMR 6011 du CNRS, Université du Maine, Avenue Olivier Messiaen, 72085 Le Mans, Cedex 9, France

ABSTRACT: The effect of plasma-induced surface crosslinking of poly(vinyl chloride) (PVC)-based flexible films was investigated to limit its migration from packaging into fatty foodstuffs. The global migration was monitored by immersion into isooctane and the specific migrations of di-2-ethylhexyladipate (DEHA) and epoxidized soybean oil (ESO) were monitored by supercritical fluid chromatography analysis of the resulting isooctane solution. The plasma induced modifications were monitored with respect to the surface energy, weight loss, and surface crosslinking. The global migration from conventionally plasticized film, whose composition corresponds to an ordinarily used formulation for the manufacture of PVC wrap films, was controlled by different plasma treatments and the best results were obtained with Ar plasma. Further decreases in global migration were obtained by treating permanently plasticized films containing an elastomeric ethylene-based terpolymer (EE) in complete or partial replacement of DEHA. Before treatment, the replacement of DEHA with EE increased the DEHA and ESO specific migrations. Argon plasma treatment of permanently plasticized films led to samples that did not exhibit any migration. © 2000 John Wiley & Sons, Inc. J Appl Polym Sci 79: 1384–1393, 2001

Key words: cold plasma; poly(vinyl chloride); global and specific migration; surface energy; crosslinking

INTRODUCTION

Contact between food and plastic packaging may cause reciprocal transfer between the material and the surrounding medium. In the case of poly(vinyl chloride) (PVC)-based commercial wrap films, various processing aids like plasticizers may exude from the packaging material or can be extracted by the foodstuff. This phenomenon (i.e., migration) causes pollution of the packaged food and a decrease of the chemical and physical properties of the plastic material.[1] In the past 20 years several articles have dealt with the interaction between the material and food, leading to the development of theories to explain migration.[2–5] But, in many cases, solutions to prevent migration have to be explored. Indeed, the legal requirements in tolerated migration and testing rules are more and more constraining.[6,7] In the PVC-based flexible food films, the migrational behavior is principally due to the low molecular

weight organic additives[5,8–10] such as di-2-ethyl-hexyladipate (DEHA) and epoxidized soybean oil (ESO).

One solution to the migration problem is the cold plasma treatment.[11] The action of plasma results in surface modification involving functionalization, degradation, and crosslinking.[12] Conditions to produce a surface crosslinked layer are expected to hinder the migration of additives.

Another way to reduce migration is to replace the low molecular weight plasticizer with an elastomeric polymer.[13] The properties of blends of PVC with elastomeric ethylene-based terpolymers[14] (EE) has gained attention, and partial or total replacement of DEHA with EE allows the production of workable flexible films.[15]

In this article we report on the results of our investigations on the cold plasma modification of flexible films with respect to the migrational properties of the resulting treated films, the surface energy increases and the crosslinking/degradation competition. Samples of a conventionally plasticized PVC film (F_1) were irradiated with various plasmas. Argon plasma treatment was also applied to permanently plasticized PVC films (F_2 and F_3) that contain EE in partial or complete replacement of DEHA.

EXPERIMENTAL

Materials

THF (99.5+%, Acros), isooctane (2,2,4-trimethylpentane, purity > 99.5%, Acros), di-2-ethylhexylphthalate (DOP, purity > 99%, Acros), and formamide (purity > 99%, Fluka) were used as received.

PVC compounds with varying contents of DEHA were supplied in a dry-blend form by Lin-Pac Plastics. The PVC was a suspension PVC with a K value of 70, and the weights per hundred parts of resin (PVC polymer) were unvarying for ESO (10 phr), metal stearates (0.88 phr), glycerol monooleate (0.8 phr), and trisnonylphenyl phosphite (0.16 phr). The EE was a poly(ethylene-co-vinyl acetate-co-carbon monoxide) (E/VA/CO, Elvaloy 742®, du Pont de Nemours) and was used as received. Migration tests and plasma treatment were realized on 14 cm^2 × 80 μm films samples.

Apparatus

The microwave plasma apparatus for irradiations consisted of three parts. The plasma exci-

tation was provided by a microwave generator (433 MHz) with a variable power output (0–250 W) coupled to a resonant cavity. The incident power (P_i) and the reflected power (P_r) were measured with a power meter (Hewlett–Packard 435B). The impedance was adjusted until the reflected power was very low ($P_r < 10^{-2}$ W). The glow was generated at the top of the reactor. The pumping system consisted of a primary pump (CIT Alcatel 2012) and an oil diffusion pump (CIT Alcatel Crystal). The gas flow (D) was controlled by an MKS mass flow meter (type 1259B). The pressure (p) was measured with Penning and Pirani gauges. The reactor was a quartz cylinder (500-mm length and 76-mm diameter). The reactor was set up on a chamber used for the sample introduction. The substrate could be treated in or out of the plasma volume. The distance (d) was measured between the bottom excitator and sample.

Supercritical fluid chromatography (SFC) was performed on Erba Science modular equipment (SFC 3000 Tandem pumping installation) comprising two electric syringe pumps, an SFC 3000 chromatograph equipped with a thermostated split semiautomatic injection system, an oven with a temperature programmer, a 15 cm × 10 mm right fused-silica tube used as a restrictor to maintain the pressure inside the column, and a flame ionization detector (FID 40). The command of the various modules, the data acquisition, and processing were carried out using an IBM PS2-30-286 microcomputer. The fluid vector was carbon dioxide.

A Rame–Hart 100-00 goniometer was used for contact angle measurements.

Plasma Treatment

The F_1, F_2, and F_3 solution cast films were obtained by solvent evaporation. THF solutions containing the PVC compounds and E/VA/CO terpolymer were mixed and the solvent was evaporated.

Before each run, the system was kept to 10^{-6} mbar for at least 2 h. After setting up the film, the reactor pressure was reduced below 2 × 10^{-5} mbar and the gas was introduced 5 min before the treatment. The standard conditions of treatment were as follows: P_i = 80 W; t = 30 s, 2 min or 5 min; D = 20 sccm; d = 20 cm; p = 0.3 mbar.

Migration Tests

The PVC film was weighed (125 mg < w_0 < 135 mg) and immersed into 50 mL of isooctane at

40°C without stirring for 2 h. The film was rinsed with isooctane, dried at 110°C for 20 min, and weighed (w_1). The isooctane solution was evaporated, and the resulting residue was dried for 24 h at 110°C.

The global migration (M_g, overall migration) was determined from the weight loss ($\Delta w = w_0 - w_1$) of the PVC film and was expressed in terms of a percentage with respect to the weights w_0 of the starting PVC film, $M_g = (\Delta w/w_0)$ %.

The amounts of DEHA (w_a) and ESO (w_e) in the residue were measured by SFC using DOP as an external standard and the following conditions: a Durabond® DB5 open tubular capillary column (100-μm i.d. and 10-m length) coated with a 0.4-μm film of diphenyldimethyl polysiloxane, an injection temperature of 40°C, an injection duration of 200 ms, a detector temperature of 300°C, an oven temperature of 60°C, and the following fluid density (δ) program:
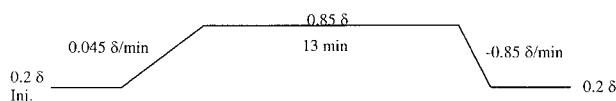
Specific migrations (M_s) were determined from the w_a and w_e of DEHA and ESO, which were solubilized in dichloromethane and expressed in terms of specific weight percentages with respect to the weights w_{a0} and w_{e0} of DEHA and ESO in the starting PVC film: $M_{s_A} = (w_a/w_{a0}) \times 100$ and $M_{s_E} = (w_e/w_{e0}) \times 100$.

Wettability Measurements

The sessile drop method was used to characterize the wettability of the plasma treated films. The contact angle Θ was determined by placing at least five drops (3 μL) of the test liquid on the polymer film. The angles were measured using a goniometer. The energetic parameters of the surface free energy (γ_s) and its dispersive and nondispersive terms (γ_s^d, γ_s^{nd}) of the polymer surface were calculated from the respective contact angles of water and formamide and the energetic parameters of water (liquid free energy, γ_L, = 72.8 mJ m^{-2}, $\gamma_L^d = 21.8$ mJ m^{-2}, and $\gamma_L^{nd} = 51$ mJ m^{-2}) and formamide ($\gamma_L = 58.2$ mJ m^{-2}, $\gamma_L^d = 39.5$ mJ m^{-2}, and $\gamma_L^{nd} = 18.7$ mJ m^{-2}).

Weight Loss and Surface Crosslinking

The weight loss was calculated from the weight of the sample before and after treatment.

The weight fraction of the THF-insoluble crosslinked part of the cast films after plasma treatment was obtained as follows: PVC film samples were immersed in 50 mL of THF; after stirring for 24 h, the insoluble fraction was filtered, washed 3 times with THF, and then dried and weighed.

RESULTS AND DISCUSSION

Gas Plasma Treatment of Conventionally Plasticized F Film

Low temperature plasma is obtained by ionization of a gas, and it operates through the interactions of energetic particles and photons with the polymer surface. The action of plasma results in crosslinking, functional group formation, and degradation (chain scission),[12] the relative importance of each phenomenon depending on the plasma generating conditions, the polymer composition, and the plasmagenic gas. Crosslinking of flexible films was expected to prevent the migration of additives. Formation of functional groups induces changes in the surface energy and wettability. Degradation induces etching and sample weight loss. In order to select the most efficient gas to prevent migration by plasma treatment, conventionally plasticized F_1 samples (see Table I for the formulation) were exposed in standard conditions to N_2, CO_2, He, H_2, or Ar plasma for 0.5, 2, and 5 min.

Beside the migrational behavior of the resulting film, the wettability and the weight loss were examined for the best understanding of the phenomenon and an industrial feasibility analysis.

Migration

The highest M_g is generally measured in fatty foodstuffs (cheese, butter); nevertheless, quantitative determination of the migrated additives in the heterogeneous foodstuff is extremely difficult. Therefore, natural migration must be simulated in model tests to determine transfers in food simulants. One of the methods commonly used to evaluate migration into fatty foodstuffs is the determination of the level of global migration from plastic into liquid oils[16] (olive oil and HB 307). Recently, solvents were suggested as simulating liquids to make the analytical procedures quicker and easier. In particular, the determination of the migration into isooctane[6] over 2 h at 40°C was

Table I   Migrational Properties, Wetting Characteristics, Weight Loss, and Insoluble Crosslinked Fraction Versus Argon Plasma Irradiation Time of Conventionally Plasticized PVC Films (F_1) and EE-Plasticized PVC Films (F_2 and F_3)

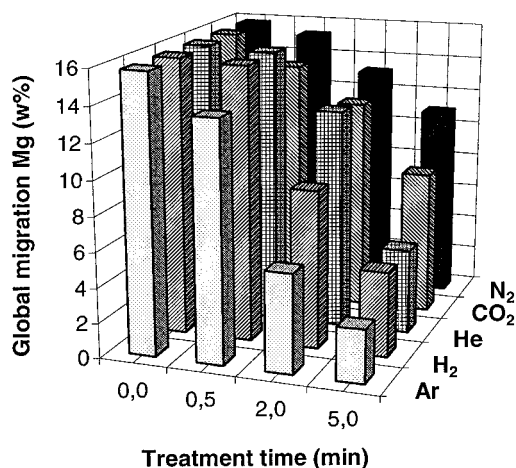| Sample PVC/ESO/ DEHA/EE Weight Ratio	Treatment Time (min)	Migrations			Wettability Characteristics				Crosslinked Fraction (wt %)	Rate of Weight Loss ($\mu g\ cm^{-2}$ min^{-1})
		$M_g{}^a$ (wt %)	$M_{s_A}{}^b$ (wt %)	$M_{s_E}{}^b$ (wt %)	Θ_w	γ_s ($mJ\ m^{-2}$)	γ_s^{nd} ($mJ\ m^{-2}$)	γ_s^d ($mJ\ m^{-2}$)		
F1 100/10/28/00	—	15.8	76	18.5	82	29.0	7.0	22.0	—	
	0.5	13.6	67	2	53	48.2	22.0	26.2	1.6	
	2	5.6	27	< 1	34	60.7	36.0	24.7	2.1	
	5	3.0	11	< 1	33	63.7	40.7	23	2.4	9.6
F2 100/10/10/40	—	10.6	95	48	82	27.5	5.2	22.3	—	
	0.5	3.3	38	8	47	55.3	32.8	22.5	0.9	
	2	0.3	20	< 1	32	62.0	38.7	23.3	1.2	
	5	0.0	< 1	< 1	23	68.4	49.9	19.5	2.1	11
F3 100/10/00/60	—	4.4	—	67	83	26.5	5.0	21.5	—	
	0.5	1.2	—	5	49	53.2	30.6	22.6	1.0	
	2	0.1	—	< 1	34	60.2	36.3	23.9	1.6	
	5	0.0	—	< 1	22	68.9	49.6	19.3	2.2	11.4

[a] The weight loss per hundred parts of sample before the test.
[b] The weight percentage of DEHA (M_{s_A}) and of ESO (M_{s_E}) that migrates from the film into isooctane.

considered as a possible equivalent to the determination into olive oil at 40°C using a contact time of 10 days.[17] Figure 1 shows the variation of the M_g into isooctane versus the plasma treatment time and plasmagenic gases.

For all the gases the M_g values decreased with increasing treatment time. Nevertheless, the Ar plasma appeared to be the most efficient: 5 min of treatment caused an M_g decrease from 15.8% to the lowest observed value (3%) and 2 min of treatment gave M_g values close to those determined

Figure 1   The global migration in plasma treated F_1 films versus the treatment time and gas.

for 5 min He or H_2 plasma treatment. It should be noted that the less efficient plasmagenic gases were CO_2 and especially N_2: 5 min of N_2 plasma treatment caused an M_g decrease from 15.8 to only 11%. These results can be correlated to several studies on polymer surface modifications dealing with the efficiency for radiative energy transfer and with the specificity of crosslinking toward functionalization or degradation. In this way, according to the better efficiency of Ar, He, and H_2 plasmas in preventing migration, it should be noted that inert gas plasmas are known to induce polymer crosslinking, Ar plasma was shown to give a higher radiative energy transfer than He plasma,[18] and H_2 plasma was shown to induce crosslinking in plasticized PVC.[19] On the contrary, according to the lower efficiency of N_2 and CO_2 plasmas, it should be noted that N_2 is known to preferentially induce the linking of functional groups and CO_2 is known to preferentially induce both degrading (chain scission) and functionalization.[12] Therefore, as previously discussed,[11] the efficiency of plasma treatment in preventing matter transfers between the material and the surrounding medium could be correlated to the formation of a 3-dimensional network on the film surface. However, a search for the best conditions implies the checking of the consequences of the treatments toward the surface energy and surface weight loss of the films.

Table II   Global Migration, Wetting Characteristics, and Weight Loss of Conventionally Plasticized F_1 Films Versus Plasmagenic Gas after 5-min Treatment

Gas	Global Migration[a] (wt %)	Wetting Characteristics				Rate of Weight Loss (μg cm^{-2} min^{-1})
		Θ_w	γ_s (mJ m^{-2})	γ_s^{nd} (mJ m^{-2})	γ_s^d (mJ m^{-2})	
BT	15.8	82	29	7	22	—
N_2	11	46	52.7	32.4	20.3	3.3
Ar	3	33	63.7	40.7	23	9.6
CO_2	8.2	22	67.7	41.7	26	26.9
He	4.8	35	62	38.6	23.4	10.7
H_2	4.8	38	60.3	36.9	23.4	12.9

BT, film characteristics before treatment.
[a] The weight loss per hundred parts of sample before the test.

Wettability and Surface Energy Modification

Wettability is one of the required properties for PVC wrap films. Indeed, it is preferred that the water vapor released by packaged food is condensed as a homogenous layer rather than as water drops on the film surface. An increase in the wettability of flexible films can be obtained by antifog additives. However, the gas plasma-induced change in the surface-functional groups results in a change of the surface wettability, which can be monitored by contact angle measurement. Contact angle measurements can be used to approach the plasma-induced surface modifications.[20–22] Indeed, the molecular approach of the surface free energy leads to the consideration of the effects of the dispersive and nondispersive forces,[22] corresponding to long-range Lifschitz–van der Waals interactions and to short-range polar interactions, respectively. Although the nondispersive component could be expressed by a donor and an acceptor part,[21] our analysis was performed considering the γ_s^d and γ_s^{nd} terms of the γ_s and using the following correlation of the contact angle with the surface energies parameters:

$$\gamma_L(1 + \cos \Theta) = 2\sqrt{\gamma_L^d \gamma_S^d} + 2\sqrt{\gamma_L^{nd} \gamma_S^{nd}}$$

Table II gives the contact angle Θ_w of the water drops with treated films versus the plasmagenic gas. The decrease of the Θ_w reflects an improvement in the degree of wetting, which can be correlated with the increase of the γ_s. Figure 2 shows the corresponding variation of the surface energy parameters γ_s, γ_s^d, and γ_s^{nd}.

Treatment for 2 min induced a noticeable increase of γ_s, but further treatment did not induce a significant variation. It should be noted that the γ_s^d remained constant and that a change in the surface energy was exclusively due to the increase of the γ_s^{nd}, corresponding to short-range polar interactions. The plasma-induced formation of functional groups was responsible for this result.
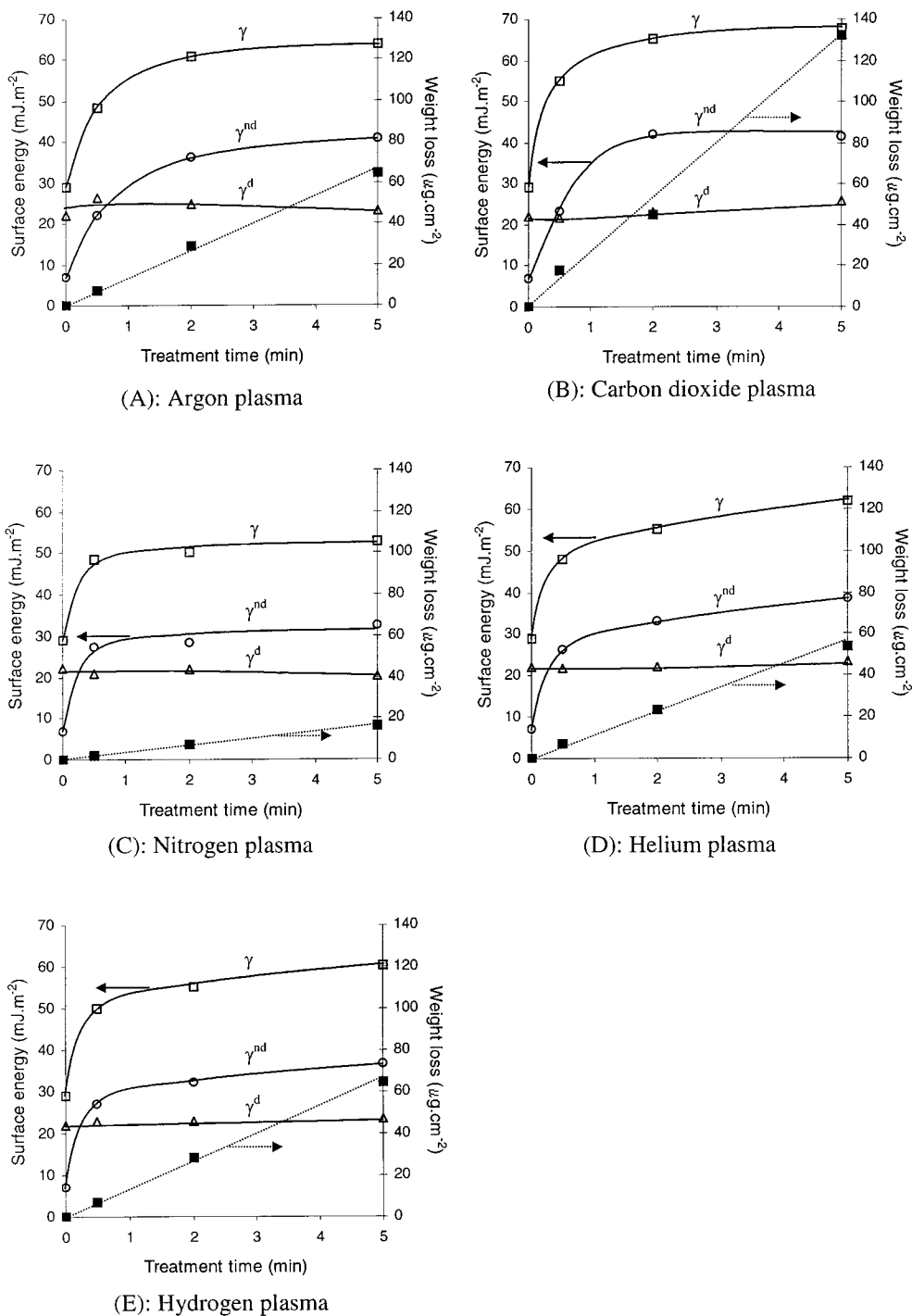
Weight Loss

Beside the surface functional group formation, the plasma treatments are known to induce ablation of matter at the surface, which is monitored by weight loss measurements. In fact, polymer degradation leads to the breakdown of a relatively small number of molecules into low molecular weight components, which eventually vaporize and are pumped out of the plasma reactor. The effect of plasma is limited to the polymer surface, and the weight loss is not dependent on the thickness of the sample. Thus, the time dependence of the weight change per surface unit can be determined for each plasma (μg cm^{-2} min^{-1}).

Figure 2 shows the linearity of the weight loss per surface unit with treatment time and Table II shows the D value for each gas. The degrading character of each gas is as follows: $N_2 <$ Ar $<$ He $<$ H $< CO_2$. The D values ranged from 3.3 mg cm^{-2} min^{-1} during N_2 plasma treatment to 26.9 mg cm^{-2} min^{-1} during CO_2 plasma treatment.

Discussion of Surface Modification/Migration Relationship

To summarize, Table II gives the global migration, the surface energy, and the weight loss of the conventionally plasticized film F_1 after 5-min plasma treatment. These results could be consid-

Figure 2   The variation of the surface energy parameters (γ_s, γ_s^d, γ_s^{nd}) and weight loss of plasma treated F_1 films versus the treatment time and gas.

ered as the expression of the chemical modification of the surface.

Carbon dioxide and N_2 plasmas are known to be chemically reactive. Crosslinking, degradation, and formation of polar functional groups oc-

cur during the treatment. The N_2 plasma was less efficient in preventing migration and improving wettability: neither crosslinking nor polar functional group formation occurred significantly in the tested conditions. The CO_2 plasma is known

to produce highly reactive atomic oxygen, giving a better control of the migration and an increase of the wettability, but the rate of weight loss was very high. A medium degree of crosslinking explains the medium M_g; the high degree of oxygen-based functional groups, allowing short-range polar interactions, explains the wettability and high γ_s^{nd} value.

Argon, He, and H_2 plasmas are known to produce surface activation by formation of unstable radicals, inducing crosslinking and degradation: when the sample was reexposed to air, reactions with oxygen led to the formation of oxygen-based functional groups. As above for the CO_2 plasma, a high content of oxygen-based functional groups explains the good wettability and high γ_s^{nd} values of the Ar, He, and H_2 plasma treated films. However, with a lower M_g value and a reasonable weight loss, the Ar plasma offers the best balance between crosslinking and degradation.

Ar Plasma Treatment of Nonconventionally Plasticized Films

A possible approach to reduce the specific migration of plasticizers from film to food is to substitute low molecular weight plasticizers (i.e., DEHA) with higher molecular weight compounds that will resist migration because of their limited mobility in the polymer matrix. Such compounds, also known as permanent plasticizers,[14] can be added to rigid PVC to reduce the glass transition of the resulting permanently plasticized material. Among them, EE is one of the most efficient permanent plasticizers; it also exhibits good compatibility with PVC.[14,15]

As a result of the decrease of the DEHA content in the F_2 and F_3 samples, the M_g was lowered below the legal requirements but the specific migrations of the low molecular weight organic additives were also increased.[15] Considering the Ar plasma treatment effect on the conventionally plasticized F_1 film, it could be reasonably expected that the migration could be reduced to a better extent by combining DEHA replacement and Ar plasma treatment.

The Ar plasma sensitivity of differently plasticized films was then investigated. Separate F_1, F_2, and F_3 samples with PVC/ESO/DEHA/EE weight ratios of 100/10/28/00, 100/10/10/40, and 100/10/0/60, respectively, were exposed to Ar plasma for 0.5, 2, and 5 min. The resulting films were tested with respect to the M_g and to DEHA and ESO specific migrations. The wettability and
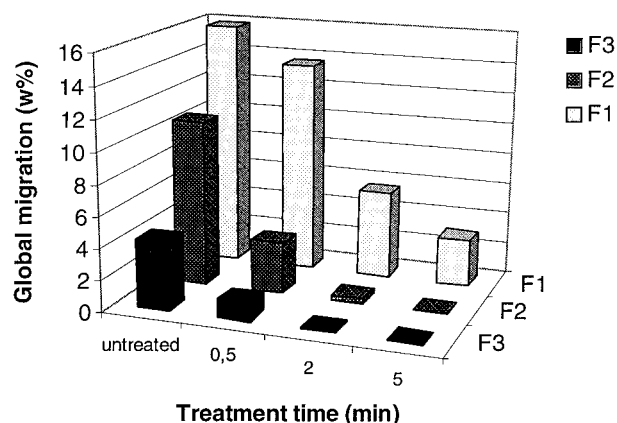
Figure 3 The global migration versus the argon plasma treatment time of conventionally plasticized film F_1 and EE-plasticized films F_2 and F_3.

weight loss determinations were completed by the evaluation of crosslinking through measurement of the THF-insoluble weight fraction.

Global and Specific Migrations

As above, the M_g was determined by the standard procedure using isooctane as the food simulant. Figure 3 shows the variation of the M_g for F_1, F_2, and F_3 samples versus the plasma treatment time. Table I gives the M_g values (column 4) as related to the sample plasticizer contents (column 2).

As expected, before treatment the M_g decreases in the order $F_1 > F_2 > F_3$. As shown and discussed elsewere,[15] this decrease in M_g is not commensurate with the decrease of the DEHA content. For each film, Ar plasma treatment induced a regular decrease of M_g with treatment time. The effectiveness of EE plasticization combined with plasma treatment is shown if we emphasize that an M_g of ~ 3 was obtained with a 5-min treatment on F_1 samples and with only a 0.5-min treatment on F_2 samples. Similarly, an M_g of < 1 was obtained with a 5-min treatment on F_2 samples and with only a 2-min treatment on F_3 samples. The plasma treatment would compensate the enhancement of the DEHA and ESO migration ability in the EE-plasticized samples.

For the best understanding, the specific migrations of DEHA (M_{s_A}) and ESO (M_{s_E}) (i.e., the weight percentage of each product that migrates from the packaging into isooctane), were found by SFC analysis. Figure 4 shows the variation of the
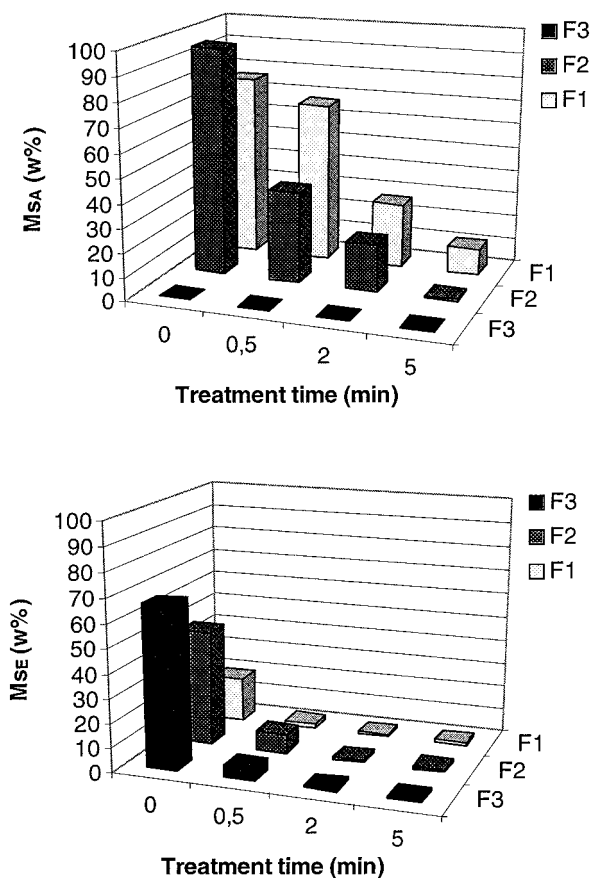
Figure 4   DEHA and ESO specific migration (M_{s_A} and M_{s_E}, respectively) in F_1, F_2, and F_3 films versus the argon plasma treatment time.

M_{s_A} and M_{s_E} from F_1, F_2, and F_3 films versus Ar plasma treatment time.

Before plasma treatment, M_{s_A} (when DEHA is present in the formulation) and M_{s_E} determined for EE-plasticized films F_2 and F_3 were higher than for conventionally plasticized film F_1. These results will be discussed elsewhere.[15] In all instances, Ar plasma treatment induced a decrease of M_{s_A} and M_{s_E} with time. The migration ability of DEHA was shown to be very sensitive to the plasma treatment. Whereas M_{s_A} was higher for F_2 than for F_1 before plasma exposure; after 0.5-min treatment the reverse order was noted. Further irradiation induced a regular decrease of M_{s_A} for both samples; the migration of DEHA was no longer observed after 5-min treatment for F_2. The migration ability of ESO was also very sensitive to the plasma treatment. The M_{s_E} values for F_2 and F_3 untreated samples were more than 2 and 3 times higher than for F_1 untreated samples, but 2-min treatment of F_1, F_2, or F_3 was sufficient to

completely hinder ESO migration. It must be noted that Ar plasma treatment appeared to be more efficient in controlling M_{s_E} than M_{s_A}. Indeed, the M_{s_E} decrease with treatment time was faster than the M_{s_A} decrease. Taking into account the molecular sizes of ESO (triglyceride with a number-average molecular weight of 960 g mol^{-1}) and DEHA (370 g mol^{-1}), this could be explained by the effect of the steric hindrance on the ability to migrate through the crosslinked layer.

Surface Modifications

In order to detect an eventual effect of the polymer composition (i.e., EE and DEHA content), the surface modifications during Ar plasma treatment were examined with respect to the variation of the surface energy parameters, weight loss, and the variation of the extent of crosslinking. Figure 5 shows the variation of the surface energy parameters γ_s, γ_s^d, and γ_s^{nd} and the weight loss of F_2 and F_3 samples versus the treatment time. The corresponding values are reported in Table I.

As observed during the Ar plasma treatment of conventionally plasticized film F_1 (Fig. 2), 2-min treatment of F_2 and F_3 samples induced a noticeable increase of γ_s and γ_s^{nd} without a variation of γ_s^d. Further treatment did not induce significant variation as observed on F_1 samples. The correlation of γ_s^{nd} with the formation of polar functional groups led to the conclusion that the DEHA and EE contents in the polymer composition had no significant consequence on the functional group formation.

Similarly to the treatment of F_1, treatment of F_2 and F_3 induced a weight loss that increased linearly with treatment time. The rates of the F_2 and F_3 weight loss (11–11.5 µg cm^{-2} min^{-1}) were only slightly higher than for F_1 (9.6 µg cm^{-2} min^{-1}), showing that the DEHA and EE contents in the polymer composition had no significant consequence on the film degradation.

The THF-insoluble fraction was used to appreciate the surface crosslinking extent.[22] The weight percent of crosslinked insoluble fraction of F_1, F_2, and F_3 samples versus the treatment time are reported in Table I (column 10). For the three films, an insoluble fraction was formed in the early stage of the treatment and its weight percentage was higher in the F_1 samples than in the F_2 and F_3 samples. The increase of the insoluble weight fraction with time made the differences between the conventionally plasticized and EE-plasticized films less important. The weight per-
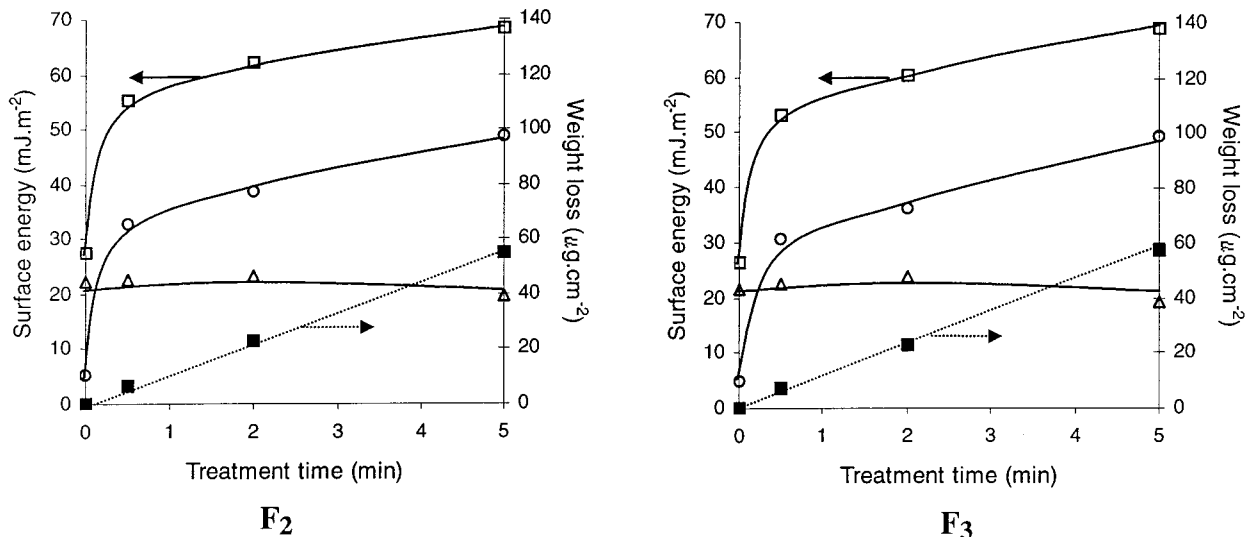
Figure 5 The variation of the surface energy parameters (γ_s, γ_s^d, γ_s^{nd}) and weight loss of argon plasma treated F_2 and F_3 films versus the treatment time.

centage of the crosslinked insoluble fraction seemed to have a ceiling value (2.4% of F_1, 2.1–2.2% of F_2 and F_3). Crosslinking would be a surface reaction, but an increase in the number of crosslinks with treatment time could raise the density of the resulting 3-dimensional network.

Discussion on Concomitant Effect of EE Plasticizing and Plasma Treatment

In agreement with a previous study,[15] the effect of DEHA replacement with EE was shown to induce a decrease of the M_g. However, the decrease of M_g from the resulting EE-plasticized films was not commensurate with the decrease of the DEHA contents in the films. Further investigations showed that the M_{s_A} and M_{s_E} from EE-plasticized films were higher than from conventionally plasticized film. The presence of EE in the film enhanced the migration ability of the low molecular weight components (i.e., DEHA and ESO).

Argon plasma induced surface modifications (crosslinking, surface energy, and weight loss) of conventionally plasticized and of EE-plasticized films varied similarly with treatment time. However, with respect to the prevention of migration, the treatment of EE permanently plasticized films was shown to be more efficient than for conventionally plasticized film: before treatment the M_{s_A} and M_{s_E} from EE-plasticized samples were higher than from conventionally plasticized films, but after Ar plasma treatment the opposite

was observed. It should be noted that the M_{s_A} was always higher than the M_{s_E} and the plasma treatment was more efficient in reducing M_{s_E} than M_{s_A}. The higher steric hindrance of ESO compared to DEHA would make its passing through the crosslinked layer more difficult. Moreover, the crosslinked layer effect on the migration can be due to the hindered penetration of isooctane into the PVC film. On this basis and regarding the steric hindrance of olive oil, the migration from plasma crosslinked film into olive oil can be expected to be lower than in isooctane. Because olive oil is recognized as a good fat simulant, the same can be expected for the migration into fatty foodstuffs.

CONCLUSION

Plasma treatment of PVC-based flexible films was shown to be able to prevent migration and improve wettability and other acceptable side modifications of the film surface. The concomitant Ar plasma treatment and replacement of a plasticizer by an adequate elastomeric polymer was shown to suppress all migrations. These results can be explained by the occurrence of a high degree of crosslinking with a reasonable degree of degradation during Ar plasma treatment and by the formation of oxygen-based functional groups when the sample was reexposed to air. Further measurements of the weight fraction of the THF-

insoluble part attested to the formation of a crosslinked layer on the polymer surface.

REFERENCES

1. Rische, S. J.; Hotchkiss, J. H., Eds. Food and Packaging Interactions II; ACS Symposium Series 473; American Chemical Society: Washington, D.C., 1988.
2. Messadi, D.; Gheid, A. E. H. Eur Polym J 1994, 30, 167.
3. (a) Papaspyrides, C. D. J Appl Polym Sci 1986, 32, 6025; (b) 1989, 38, 1859; (c) 1992, 44, 1145.
4. Messadi, D.; Djilani, S. E. Eur Polym J 1998, 34(516), 815.
5. Vergnaud, J. M. Liquid Transport Processes in Polymeric Materials—Modeling and Industrial Applications; Prentice Hall: Englewood Cliffs, NJ, 1991.
6. (a) EEC. Offic J Eur Commun 1982, October 23, L 297; (b) EEC. Offic J Eur Commun 1989, February 11, L 40; (c) EEC. Offic J Eur Commun 1997, July 29.
7. U.S. FDA. Recommendations for Chemistry Data for Indirect Food Additive Petitions; U.S. FDA: Washington, D.C., 1995.
8. Harrison, N. Food Additives Contam 1988, 5, 493.
9. Gilbert, J.; Castle, L.; Jickells, S. M.; Mercer, A. J.; Sharman, M. Food Additives Contam 1988, 5, 513.
10. Kampouris, E. M.; Regas, F.; Rokotas, S.; Polychronakis, S.; Pantazoglou, M. Polymer 1975, 16, 840.
11. Iriyama, Y.; Yasuda, H. J Appl Polym Sci Appl Polym Symp 1988, 97, 97.
12. Brosse, J. C.; Legeay, G.; Poncin-Epaillard, F. In Desk Reference of Functional Polymers; Arshady, R., Ed.; American Chemical Society: Washington, D.C., 1997; p 201.
13. Huang, C.; Chen, J. Polym Plast Technol Eng 1994, 33, 615.
14. (a) Bair, H. E.; Anderson, E. W.; Johnson, G. E.; Kwei, T. K. Polym Prepr 1978, 19, 143; (b) Hein, M. D. J Vinyl Technol 1994, 16, 208.
15. Audic, J. L.; Brosse, J. C.; Reyx, D. Unpublished results.
16. Figge, K.; Hilpert, H. A. Dtsch Lebensm Rundsch 1991, 87, 1.
17. De Kruijf, N.; Rijk, M. A. H.; Soetardhi, L. A.; Rossi, L. Food Chem Toxicol 1983, 21, 187.
18. Clouet, F.; Shi, M. K. J Appl Polym Sci 1992, 46, 1955.
19. (a) Zahran, A. H.; Nofal, E. J Appl Polym Sci 1979, 24, 1723; (b) Zahran, A. H.; Nofal, E. J Appl Polym Sci 1979, 24, 1875.
20. Good, R. J. J Adhes Sci Technol 1992, 6, 1269.
21. Hollander, A.; Behnisch, J.; Zimmermann, H. J Polym Sci Part A Polym Chem 1994, 32, 699.
22. Poncin-Epaillard, F.; Vallon, S. Macromol Chem Phys 1997, 198, 2439.