Optimization of a Process Capable of Decreasing the Pollution from PVC Packaging Material

ALI BICHARA, JEAN-LUC FUGIT, ISABELLE OUILLON, JEAN-LOUIS TAVERDET

Laboratoire Chimie et Environnement, Faculté des Sciences et Techniques,

23, rue du Docteur Paul Michelon, 42023 Saint-Etienne cedex 2, France

ABSTRACT: This work is the study of a process capable of decreasing the migration of the plasticizer into a liquid food or a simulant from a plasticized PVC packaging. The treatment is a two-step process: (1) soaking in a liquid, and (2) drying at various temperatures. The efficiency of this method depends on many factors: nature of the liquid and immersion time, temperature and time of drying, etc. The influence of the most important of them had been quantified with a mathematical model previously described. The purpose of this study is to search for the best value of each parameter and, therefore, to optimize the reduction of mass transfers. © 1999 John Wiley & Sons, Inc. J Appl Polym Sci 74: 3492–3450, 1999

Key words: plasticized PVC; mass transfers; food simulants; decrease of pollution; DEHP

INTRODUCTION

Poly(vinyl chloride) is extensively used for the packaging used in food items and pharmaceuticals. It is also used for the manufacture of blood bags, urine bags, transfusion tubings, etc. In fact, it is one of the most widely used polymeric materials in the medical field.[1–3]

However, this plastic contains a number of additives (antioxydant, antistatic agent, lubricant, plasticizer, etc.) to improve its physical and mechanical properties. For example, plasticizers are incorporated into polymer to increase workability, flexibility, and extensibility. Because of its excellent compatibility with poly(vinyl chloride) (PVC), di-2-ethyl-hexyl-phtalate (DEHP) is often used. Probably it is the most important low-cost commercial plasticizer. PVC used in medical applications contains up to 65 phr of DEHP.

Unfortunately, when plasticized PVC is in contact with a liquid (food, pharmaceuticals, blood, etc.) a simultaneous transfer of the liquid into (labeled counterdiffusion) and plasticizer out takes place with the following results:[4–9] the liquid is polluted by the plasticizer, and there is a decrease in physical properties of the plastic. Furthermore, the higher the initial plasticizer content, the more important the mass transfers.

Various attempts have been made to decrease plasticizer transfer from plasticized PVC. For example, the PVC surface is coated with polymers such as acrylates or polyesters, or the PVC is crosslinked during processing with peroxides; one can also graft hydrophilic monomers on to the surface of PVC by gamma radiation and plasma treatment of PVC surface.[10–13] More recently,[14–16] it was shown that coating the PVC surface with azidated PVC and photocrosslinking UV irradiation or photocrosslinking of dithiocarbamate-substituted PVC can reduce the plasticizer migration.
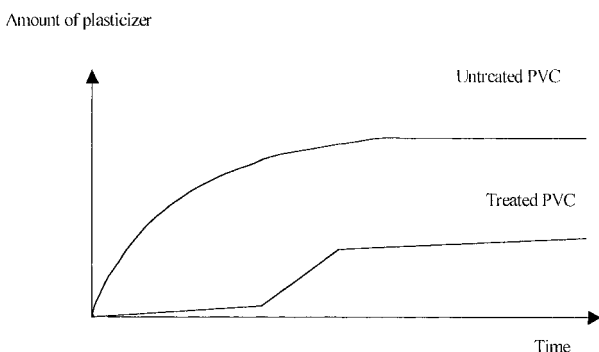
Figure 1 Profile of the curve: amount of plasticizer vs. time according to treated or untreated PVC.

In a previous work[8,17] we described a method for obtaining a plasticized PVC exhibiting low mass transfer. It is a two-step process: (1) plasticized PVC with DEHP is immersed in a liquid for a short time (e.g., 2 min); and (2) then the PVC, extracted from the liquid, is dried (e.g., 5 min at 90°C).

With the PVC having been subjected to the treatment, the transfers of liquid and plasticizer are both delayed and reduced when the treated PVC is soaked again in the same liquid or another one. Figure 1 shows the shape of the curves that represent the fraction of DEHP lost with treated and nontreated PVC.

An explanation of this phenomenon and a model capable of quantifying the rate of mass transfers in terms of diffusivity have been proposed in a recent article.[18] The efficiency of the treatment depends on many parameters: time and temperature of soaking during the first step, time and temperature of drying, and the concentration of plasticizer of the original PVC. The goal of this article is to determine the best value for the parameters having a great influence on the decrease of the mass transfers. We have also studied an important parameter: the nature of the liquid used in the first stage of the treatment, because with some liquids there is pratically no effect on the migration.

EXPERIMENTAL

Materials

The analyses of DEHP in the liquid were performed by gas chromotography (Intersmat IGC 16) after an addition of Di-ethyl-hexyl-adipate as an internal standard. The stationary phase is Chromosorb Q and 2.5% OV 17 silicone rubber (Dow Chemical). Determination of DEHP released was carried out also on a JASCO UV-VIS apparatus at the corresponding λ_{max}. The amount of liquid entering the PVC was determined by weighing the PVC disk at the same time as the DEHP was measured. The glass transition temperature of the plasticized PVC was performed by DSC 92 Setaram.

Chemicals

PVC is a commercial resin (Fluka) in the form of a white powder ($M_n = 25,900$ g · mol^{-1} and $M_w = 54,800$ g · mol^{-1}).

Di-2-ethyl-hexyl-phtalate (Prolabo), Di-ethyl-hexyl-adipate (Sigma), n-heptane (Flucka), absolute ethanol (SDS), and absolute methanol (Sigma), acetic acid (Accros), and acetone (Flucka) were used as received.

Preparation of the Plasticized PVC Samples

Plasticizer (DEHP) and PVC were mixed in methanol to obtain a homogeneous mixture. Then, methanol is completely evaporated at 60°C.

The various compounds (PVC + DEHP) have been pressed into sheets in a steel mold at 150°C and under a pressure of 100 bars. Discs of 13 (or 18) mm in diameter and 1 (or 3) mm thick have been cut from these PVC sheets.

Preparation of the PVC Samples with Low Mass Transfers

First stage: PVC disks were soaked in a liquid for a short period of time (e.g., 2 min). The liquid was n-heptane, or another one. Second stage: the disks were dried at various temperatures (from 20 to 100°C) and for various periods of time (from 2 to 8 min).

In fact, the PVC disks were placed in an atmosphere at fixed temperature. Figure 2 indicates the real temperature level reached by the PVC faces as a function of time. It should be noticed that the PVC faces are at the surrounding temperature level after about 4 min. The temperature was determined with a fine thermocouple (type T, diameter: 0.254 mm, from OMEGA).

Test for Determining the Rate of Plasticizer and Liquid Transfer

To test the efficacy of the treatment, treated or untreated PVC was soaked in a liquid according to the operative conditions described below.
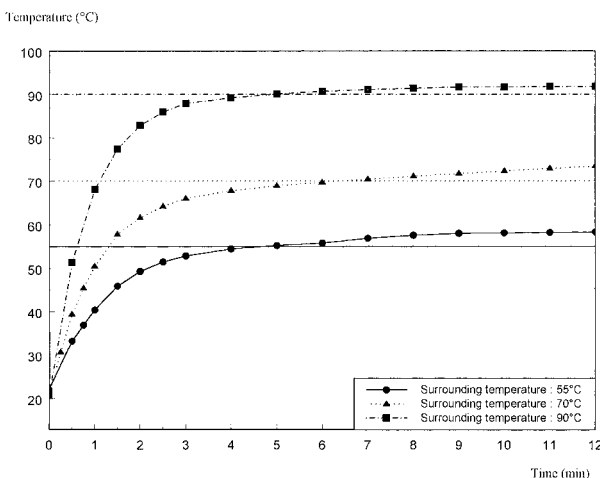
Figure 2 Temperature of the PVC faces as a function of time, when the PVC sample was placed in an atmosphere at various temperatures.

Diffusion experiments (labeled "last stage" or "migration test") were conducted in a closed flask (50 cm^3), kept at 20 or 30°C, and at a controlled stirring rate. One PVC disk was immersed in 20 cm^3 of liquid (n-heptane, arachid oil, ethanol, acetic acid, and acetone).

At different times, the plasticizer was analyzed in the liquid and the disk was weighed to determine the liquid quantity entering the PVC. Experiments were repeated three times, and each experiment exhibited similar results because of the good homogeneity of the plasticized PVC sheets.

THEORETICAL

The model used to quantify the diffusion rate (whose main chraracteristics are recalled herein) has been described in a recent article.[18] In this model, the treated PVC is considered like a sandwich material: the original PVC between two sheets of PVC without plasticizer and without liquid. The mass transfers rates are limited by the slowest step: the diffusion in the glassy PVC layer. The assumptions and the mathematical treatment allow us to calculate two diffusivities: (1) an average diffusion coefficient D_1 with the relationship

$$D_1 = \frac{\ell^2}{6 \cdot t_d} \tag{1}$$

where t_d is the time lag and ℓ the thickness of the membrane (layer of rigid PVC). (2) A diffusivity D_2 obtaining during the steady state of the transfer

$$D_2 = \frac{P \cdot \ell}{C} \tag{2}$$

C being the mass of DEHP per volume unit in the original PVC; P being the slope of the straight line of the curve that represents the loss of DEHP vs. time.

The value of D_2 is the greater value of this coefficient, because at this moment (steady state) the membrane is saturated with liquid and DEHP.

To estimate the efficacy of the method we also determine the diffusion coefficient D_0 of the migrant species (liquid or plasticizer) with the untreated PVC in the first stage of the process. It is calculated with the approximated equation valid for the short times.[19]

$$\frac{M_t}{M_\infty} = 4 \cdot \left(\frac{D_0}{\Pi \cdot e^2} \right) \tag{3}$$

where e is the whole thickness of the disk, M_t the amount of migrant species (liquid or plasticizer) at time t, and M_∞ the corresponding amount at equilibrium.

RESULTS AND DISCUSSION

The effectiveness of the process depends on many parameters. The achieved experiments have been chosen to determine their best value and, therefore, to optimize the process, but also to have access to a better understanding of the transport mechanism in polymers.

Influence of the Inherent Factors of the First Stage

Nature of the Immersing Liquid

Various liquids have been used to study the influence of the nature of the liquid during the first stage of the process. They have been chosen because of their different properties: molecular volume, function (alcohol, acid, etc.), volatility, etc. These food or food simulant liquids are: n-heptane, ethanol, methanol, ethanoïc acid, acetone, and arachid oil.
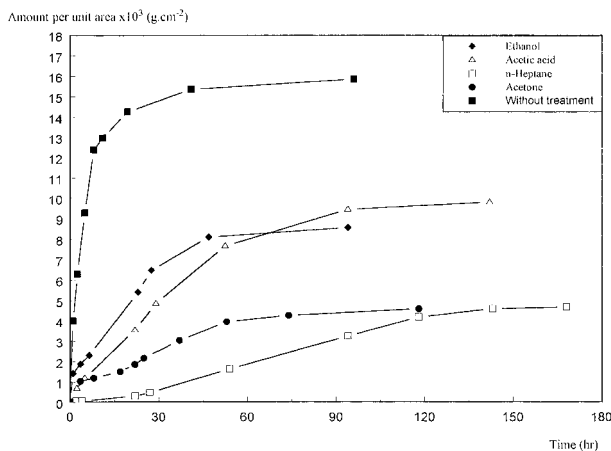
Amount per unit area x10³ (g·cm⁻²)

Figure 3   Amount of DEHP per unit area vs. time, as a function of the immersing liquid during the first stage. The PVC is initially plasticized at 35% and $e = 1$ mm. All treated specimens are dried at 100°C for 5 min. The liquid of the "test migration" is always ethanol. ■ Untreated PVC; △ first soaking in ethanol for 16 min; ◆ first soaking in acetic acid for 16 min; ● first soaking in acetone for 16 min; □ first soaking in n-heptane for 16 min.

The experiments are achieved according to the following conditions: PVC originally plasticized with 35% of DEHP is soaked for 16 min in n-heptane, ethanol, methanol, acetone, and acetic acid. The sample of PVC is extracted from the liquid and dried for 5 min at 90°C. Finally, the treated PVC is immersed again in pure ethanol to test the efficacy of the treatment.

From our experimental results (Fig. 3) we can make the following observations:

1. The process is really effective only with n-heptane and acetone. Others results[8] have shown that the reduction of mass transfer is also effective with other alcanes. Indeed, in this case, the migration of DEHP is delayed, slackened, and reduced.

2. No sensitive effect has been observed with another liquid, such as acetic acid, alcohols, etc. Indeed, there is no intervall of time during which no transfer occurs, and the curve amounts of DEHP vs. time are the same shape as with untreated PVC. However, the amount of DEHP released at equilibrium is smaller with treated PVC than untreated PVC. These results are in accord with the ones obtained by Papaspyrides,[20] who studied the effect of sample history (soaking of PVC in paraffin oil) on the dioctyl phtalate

from plasticized PVC immersed in petro-leums oils.

3. In addition, in a previous work,[8] we have already observed that a PVC first soaked in arachid oil and dried at surrounding temperature, has practically the same behavior as untreated PVC. In other words, there is no difference between the curve giving the amount of migrant species as a function of time with untreated PVC and the curve with treated PVC.

These results are of interest because they demonstrate that the liquid that enters the PVC plays a major role in the mechanism of such transfers. But, what explains the differences between the behavior of these liquids? We can bring some answers to this phenomenon.

1. As we already said in a previous work,[18] the drying stage allows the removal of the liquid from the PVC surfaces and, therefore, to obtain a layer practically without DEHP and without liquid. Therefore, if we compare arachid oil, whose boiling point is high, and heptane, (temperature of ebullition equal to 98°C) it is obvious that arachid oil does not evaporate during the second stage, and therefore, there is no formation of glassy PVC membrane because arachid oil plays the role of plasticizer. Thus, there is practically no change in the rate of mass transfers when the sample of treated PVC is soaked again in liquid.

2. With ethanol or methanol (whose boiling point is not high and even lower than heptane) the problem is more complex. It may be that interaction forces exist between DEHP and alcohol (e.g., hydrogen bonds). Therefore, during the second stage, only one part of the liquid is eliminated, as with other liquids; but in this case, ethanol or methanol, bonded with DEHP, carries plasticizer away on the surface and the membrane stays partially plasticized. In addition ethanol (or methanol) is a better plasticizer than heptane. Besides, the PVC disks, containing ethanol instead of DEHP (e.g., at equilibrium), are softer and more flexible than those containing n-heptane. In conclusion, it seems that the best liquid to use in the first stage must possess properties similar to n-heptane: relatively volatile and a little affinity with plasticizer.

Table I   Solubility Parameters of PVC, DEHP, and Various Liquids

	δ (J · cm^{-3})$^{1/2}$	δ_d (J · cm^{-3})$^{1/2}$	δ_p (J · cm^{-3})$^{1/2}$	δ_h (J · cm^{-3})$^{1/2}$
PVC	22.5	19.2	9.2	7.2
DEHP	18.2	16.6	7	3.1
n-Heptane	15.2	15.2	0	0
Acetone	20.1	15.5	10.4	7
Methanol	29.7	15.1	12.3	22.3
Ethanol	26.6	15.8	8.8	19.4
Acetic acid	21.3	14.5	8	13.5

The solubility parameters are given by the literature.[1,21,22]

3. Is this experimental conclusion (i.e., heptane is the most efficiency liquid) can be connected with solubility parameters δ? Indeed these parameters are important quantities in all phenomena involving interactions between polymers and solvents or plasticizers. Table I that gives these quantities for PVC, DEHP, and various liquids[1,21,22] show no obvious correlation between experimental results and solubility parameters. However, it should be pointed out that the liquids having no sensitive effect (as acetic acid, alcohols, etc.) have a solubility parameter component δ_h (in relation with hydrogen bonding) with a great value, while the efficacy liquid as *n*-heptane (others alcanes and acetone) have a δ_h with a small value as the plasticizer and PVC. This observation confirms the previous hypothesis saying that a efficacy liquid does not have strong interaction forces between DEHP and polymer because it is not eliminated from the plastic during the second stage of the process.

Time of the First Soaking

We have seen[18] that the time of the first stage is a factor having a great influence on the process because it determines the thickness of the membrane (i.e., the film practically without DEHP). Figure 4 represents the time of delay (i.e., the time during which there is no mass transfer when treated PVC is soaked in *n*-heptane) vs. the immersing time in heptane at 20°C and when the plasticized PVC (50% with DEHP) has been dried at 90°C and for 5 min. This figure indicates that the time lag is roughly proportional to the immersing time. In addition, the increase of this time reduces the amount of DEHP released at equilibrium. Therefore, the process is more efficient when we increase the time of the first stage. This result is confirmed by Table II, which gives the diffusivities and the time lag of DEHP corresponding to the previous experiment. However, one cannot extend this time indefinitely, because PVC will lose its properties at the same time as plasticizer will leave the plastic. In conclusion, the best value of this factor must be determined according to the needs of the finished product.

Influence of the Inherent Factors of the Second Stage (Drying)

Temperature

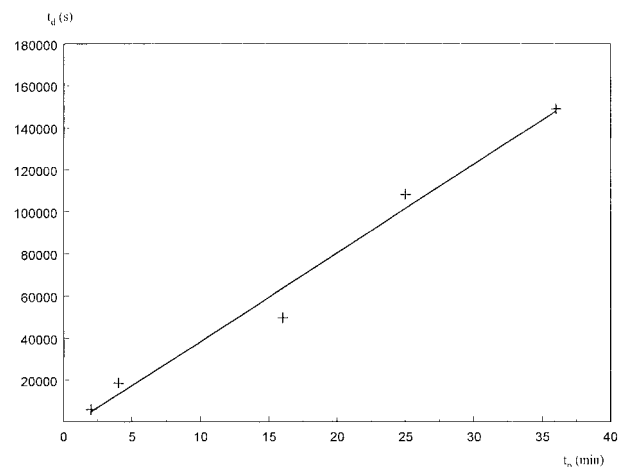In the experiments presented in this paragraph, we have used PVC plasticized with 35 or 50% (in

Figure 4   Time lag vs. the time of immersion during the first stage of the treatment. The liquid is *n*-heptane during the first stage like during the test migration. The transfer temperature is always 20°C. The PVC (initially plasticized at 50% with DEHP) is dried at 90°C for 5 min. $e = 1$ mm.

Table II   Influence of the First Soaking Time on the DEHP Migration

Time of Soaking (Minutes)	Time Lag t_d (s)	D_0 (cm$^2 \cdot$ s^{-1})	D_1 (cm$^2 \cdot$ s^{-1})	D_2 (cm$^2 \cdot$ s^{-1})
2	5800	3.3 10^{-7}	8.8 10^{-10}	12.0 10^{-9}
4	18,500	3.3 10^{-7}	5.1 10^{-10}	9.4 10^{-9}
16	49,800	3.3 10^{-7}	8.0 10^{-10}	3.0 10^{-9}
25	108,100	3.3 10^{-7}	5.9 10^{-10}	2.8 10^{-9}
36	148,700	3.3 10^{-7}	6.5 10^{-10}	4.7 10^{-9}

PVC initially plasticized at 50% with DEHP ($e = 1$ mm) is previously treated under the following operative conditions: (1) first soaked in n-heptane at 20°C for various times; (2) dried at 90°C for 5 min. The migration test is achieved with n-heptane at 20°C.

weight) of DEHP. The liquid is n-heptane in the first stage of the experiment like in the last one. During the step of drying, the PVC disk, initially at 20°C, is placed in an atmosphere at various temperatures (55, 70, 80, 90, and 100°C) and for 5 min. The faces of the PVC disk reach the final temperature, as indicated by Figure 2 (see the Experimental section).

The results obtained in this study (Fig. 5, Table III) show that increasing the temperature does not have a great influence on the diffusivities, but increases the time lag both of the plasticizer loss and the entering of liquid, on conditions not to exceed 90°C. Indeed, when the drying temperature exceeds 90°C, the efficacy of the process decreases. This observation is true with PVC plasticized at 35% as PVC plasticized at 50%. One can explain these facts in the following way. The raising of drying temperature accelerates the removal of liquid at the same time as the rearrangement of macromolecular chains. Therefore, the layer having lost its plasticizer and its liquid (at least partially) becomes more rapidly and more efficiently a membrane of glassy PVC, than at room temperature. But increasing temperature also increases

the mobility of DEHP (staying in the core of the disk), and the plasticizer can migrate into the membrane and plasticize it again. One can suppose that this last phenomenon becomes predominant after 90°C, while the formation of glassy PVC layer is more favored before this temperature. As a result, the best value of the drying temperature seems to be 90°C, at least under the other operative conditions fixed in these investigations.

Duration of Drying at 90°C

To study the influence of the time of the second step of the process, we have used, as previously, PVC plasticized with 50% of DEHP, soaked first in heptane for 4 or 16 min at 20°C. Then the PVC sample was placed in an atmosphere at 90°C for various times: 2, 3 , 4, 5, and 8 min. Finally, PVC was immersed again in n-heptane. Figure 6(A) and (B), which represent the time lag against the duration of drying, show that the treatment was more efficace when the drying lasted 4 min. Table IV, giving the diffusivities D_1 and D_2, confirms this result. This observation is valid whatever the

Table III   Influence of the Drying Temperature on the DEHP and n-Heptane Migration

Drying Temperature (°C)	Time Lag t_d (s)		D_0 (cm$^2 \cdot$ s^{-1})		D_1 (cm$^2 \cdot$ s^{-1})		D_2 (cm$^2 \cdot$ s^{-1})	
	DEHP	n-heptane	DEHP	n-Heptane	DEHP	n-heptane	DEHP	n-Heptane
55	8700	5400	3.3 10^{-7}	5.2 10^{-6}	1.1 10^{-9}	1.8 10^{-9}	9.0 10^{-9}	2.4 10^{-8}
70	13,400	8600	3.3 10^{-7}	5.2 10^{-6}	7.5 10^{-10}	1.2 10^{-9}	1.1 10^{-8}	2.5 10^{-8}
80	13,800	9700	3.3 10^{-7}	5.2 10^{-6}	6.7 10^{-10}	9.6 10^{-10}	9.7 10^{-9}	2.1 10^{-8}
90	17,300	10,500	3.3 10^{-7}	5.2 10^{-6}	4.9 10^{-10}	8.0 10^{-10}	6.3 10^{-9}	1.7 10^{-8}
100	9700	2580	3.3 10^{-7}	5.2 10^{-6}	8.9 10^{-10}	3.4 10^{-9}	5.1 10^{-9}	1.3 10^{-8}

PVC initially plasticized at 50% with DEHP ($e = 1$ mm) is previously treated under the following operative conditions: (1) first soaked in n-heptane at 20°C for 4 min; (2) first dried for 5 min at various temperatures. The migration test is achieved with n-heptane at 20°C.
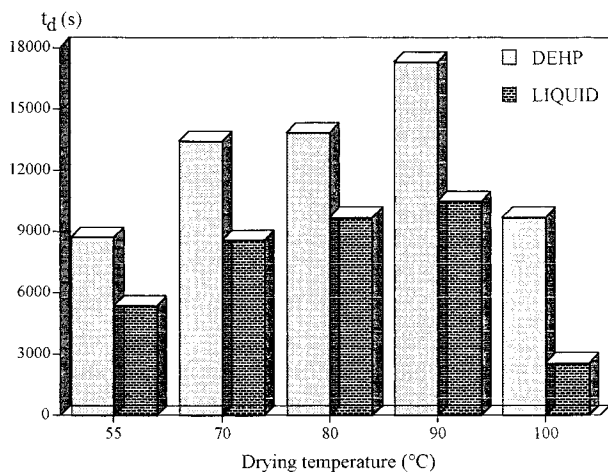
A
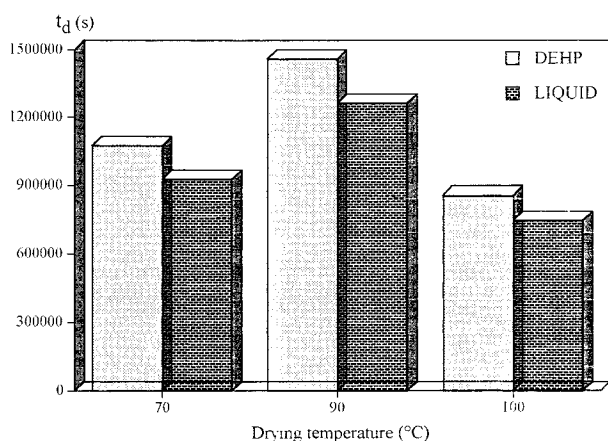
B

Figure 5 Time lag vs. the drying temperature. The liquid medium is *n*-heptane during the first stage like the test migration. The transfer temperature is 20°C. (A) PVC initially plasticized at 50% (e = 1 mm) is first soaked for 4 min, then dired for 5 min at various temperature levels. (B) PVC initially plasticized at 35% (e = 1 mm) is first soaked for 21 min, then dried for 5 min at various temperature levels.

time of the first immersion. The explanation of this phenomenon is similar to the one given in the previous section. Indeed, two opposite phenomena take place simultaneously: the formation of the membrane of glassy PVC, and the migration of DEHP from the core of the disk. The former improves the efficacy of the barrier, while the latter decreases the waterproof qualities, because DEHP, arriving from the core, again plasticizes the layer near the surface. Up to 4 min, the first phenomenon is predominant, while after this time it is the DEHP migration that has the better of the barrier formation. Therefore, it seems that

the best value of the drying time is about 4 min at 90°C.

Influence of the Inherent Factors of the Test Migration

Nature of the Lquid

The influence of this parameter had been investigated with a plasticized PVC (35% in weight) having been subjected to the following treatment: soaking for 30 min in *n*-heptane at 30°C and then drying for 2 h at surrounding temperature. Then the treated PVC samples were immersed in dif-
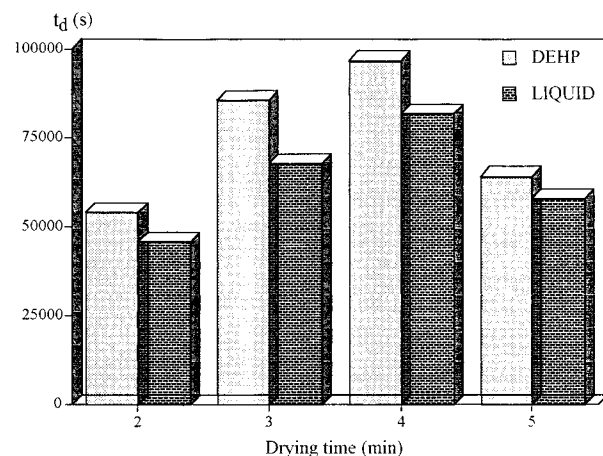
A
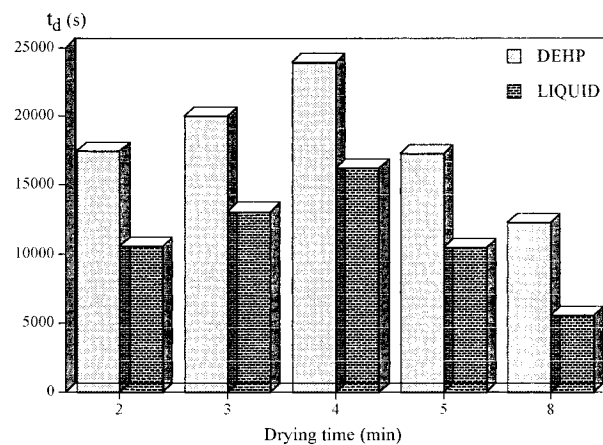
B

Figure 6 Time lag vs. the drying time. The liquid used is *n*-heptane during the first stage like the last one. The transfer temperature is 20°C. (A) PVC initially plasticized at 50% (e = 1 mm) is first soaked for 16 min, then dried for various periods of time at 90°C. (B) PVC initially plasticized at 50% (e = 1 mm) is first soaked for 4 min, then dried for various periods of time at 90°C.

Table IV   Influence of the Drying Time on the DEHP and *n*-Heptane Migration

Drying Time (Minutes)	Time Lag t_d (s)		D_0 (cm$^2 \cdot$ s^{-1})		D_1 (cm$^2 \cdot$ s^{-1})		D_2 (cm$^2 \cdot$ s^{-1})	
	DEHP	*n*-heptane	DEHP	*n*-heptane	DEHP	*n*-heptane	DEHP	*n*-heptane
2	17,500	10,600	$3.3 \ 10^{-7}$	$5.2 \ 10^{-6}$	$5.6 \ 10^{-10}$	$9.2 \ 10^{-10}$	$6.7 \ 10^{-9}$	$1.6 \ 10^{-8}$
3	20,000	13,100	$3.3 \ 10^{-7}$	$5.2 \ 10^{-6}$	$4.9 \ 10^{-10}$	$7.5 \ 10^{-10}$	$5.5 \ 10^{-9}$	$1.7 \ 10^{-8}$
4	23,900	16,300	$3.3 \ 10^{-7}$	$5.2 \ 10^{-6}$	$3.8 \ 10^{-10}$	$5.6 \ 10^{-10}$	$5.7 \ 10^{-9}$	$1.7 \ 10^{-8}$
5	17,300	10,500	$3.3 \ 10^{-7}$	$5.2 \ 10^{-6}$	$4.9 \ 10^{-10}$	$8.0 \ 10^{-10}$	$6.3 \ 10^{-9}$	$1.7 \ 10^{-8}$
8	12,300	5600	$3.3 \ 10^{-7}$	$5.2 \ 10^{-6}$	$8.5 \ 10^{-10}$	$1.9 \ 10^{-9}$	$7.4 \ 10^{-9}$	$1.7 \ 10^{-8}$

PVC initially plasticized at 50% with DEHP ($e = 1$ mm) is previously treated under the following operative conditions: (1) first soaked in *n*-heptane at 20°C for 4 min; (2) dried at 90°C for various periods of time. The migration test is achieved with *n*-heptane at 20°C.

ferent liquids. Table V, which gives the time lag and the diffusivities of DEHP with *n*-heptane and arachid oil, shows that the influence of the liquid of the last step is the same as the original plasticized PVC. Indeed, the diffusivity decreases and the time lag increases when the molecular size becomes greater. However, with the treated PVC samples, the diffusivity of DEHP (or liquid) is far more smaller than with original PVC, whatever the liquid used.

Nevertheless, from our work, it seems that the treatment is optimal when *n*-heptane is used during the first stage of the process.

Temperature

In all investigations that we carried out, the increasing of temperature decreases the efficacy of the treatment. Table VI,which reports the results obtained with a PVC previously immersed in heptane for 2 or 4 min, dried at 90°C for 5 min and soaked again in *n*-heptane, shows that the time lag decreases and the diffusivities increase when the temperature of migration test is 50°C instead of 20°C. Similar results are obtained with other liquids and other treated PVC, and are in agreement with the fact that temperature increases the

diffusion in polymers[6,23–27] according to Arrhenius' law.

CONCLUSION

This work shows that it is possible to make a plasticized PVC exhibiting low mass transfer, even with a strong percentage of plasticizer. Many factors can have a great influence on the reduction of migration, and the effects of these parameters have been investigated to improve the efficacy of the treatment.

Therefore, from this study, it can be concluded that there is a big difference on the mass transfer reduction according to the liquid used in the first stage. The achieved experiments showed, once again, that the counterdiffusion (penetrating liquid) plays a fundamental role in the additives diffusion out of polymers. Indeed, in accord with other results,[6,8,28–30] the transfer of both liquid and plasticizer are intimately connected. From our work, *n*-heptane seems to be the most efficient liquid.

The time and the temperature of the second stage (drying of sample) are also two important

Table V   Influence of the Nature of the Immersion Liquid in the Migration Test on the DEHP Diffusion

Liquid	Time Lag t_d (s)	D_0 (cm$^2 \cdot$ s^{-1})	D_1 (cm$^2 \cdot$ s^{-1})	D_2 (cm$^2 \cdot$ s^{-1})
Arachid oil	1,500,000	$1.3 \ 10^{-9}$	$2.9 \ 10^{-11}$	$5.2 \ 10^{-11}$
n-Heptane	74,000	$9.0 \ 10^{-8}$	$5.1 \ 10^{-10}$	$2.0 \ 10^{-9}$

PVC initially plasticized at 35% with DEHP ($e = 3$ mm) is previously treated under the following operative conditions: (1) first soaked in *n*-heptane at 30°C for 0.5 h; (2) dried at surrounding temperature for 2 h. The migration test is achieved with various liquids at 30°C.

Table VI   Influence of the Temperature (T_r) on the DEHP Migration Test

Time of Soaking (Minutes)	T_r (°C)	Time Lag t_d (s)	D_0 (cm$^2 \cdot$ s^{-1})	D_1 (cm$^2 \cdot$ s^{-1})	D_2 (cm$^2 \cdot$ s^{-1})
2	20	5800	3.3 10^{-7}	0.9 10^{-9}	1.2 10^{-8}
2	50	2660	3.3 10^{-7}	2.0 10^{-9}	1.9 10^{-8}
4	20	18,500	3.3 10^{-7}	0.5 10^{-9}	0.9 10^{-8}
4	50	4000	3.3 10^{-7}	10.4 10^{-9}	2.1 10^{-8}

PVC initially plasticized at 50% with DEHP (e = 1 mm) is previously treated under the following operative conditions: (1) first soaked in n-heptane at 20°C for various periods of time; (2) dried at 90°C for 5 min. The migration test is achieved with n-heptane at various temperatures.

factors. Indeed, the interval of time during which no transfer occurs, increases strongly with these parameters, on condition not to exceed 90°C and 4 min.

The efficacy of the method also depends on the nature of the liquid used in the test migration. For example, the time lag can reach about 17 days if the treated PVC is immersed in arrachid oil, while with heptane and with the same treated PVC the delay time is only 1 day.

Finally, these results confirm that the temperature at which the food or pharmaceuticals must be preserved has to be as low as possible.

REFERENCES

1. Sears, J. K.; Darby, J. R. The Technology of Plasticizers; Wiley-Interscience: New York, 1982.
2. Gächter, R.; Müller, H. Plastics Additives Handbook; Hanser Publishers: New York, 1993.
3. Hanlon, J. F.; Kelsey, R. J.; Forcinio, H. E. Handbook of Package Engineering; Technomic Publication: Lancaster, PA, 1998.
4. Haesen, G.; Schwarze, A. Commission of European Communities; Petten: Holland, 1978.
5. Figge, K. Prog Polym Sci 1980, 6.
6. Messadi, D.; Taverdet, J. L.; Vergnaud, J. M. I EC Prod Res Dev 1983, 22.
7. Taverdet, J. L.; Vergnaud, J. M. J Appl Polym Sci 1984, 29, 3391.
8. Taverdet, J. L. Thesis, University of Saint-Etienne, France (1985).
9. Blais, P. Can Res 1981, 13, June, July.
10. Duvis, T.; Karles, G.; Papaspyrides, C. D. J Appl Polym Sci 1991, 42, 191.
11. Krishnan, U. K.; Jayakrishnan, A.; Francis, J. D. J Mater Sci Mater Med 1990, 1, 185.
12. Krishnan, U. K.; Jayakrishnan, A.; Francis, J. D. Biomaterials, 1991, 12, 489.
13. Iryama,Y.; Yasuda, H. J Appl Polym Sci Appl Polym Symp 1988, 42, 97.
14. Jayakrishnan, A.; Sunny, M. C.; Rajan, M. N. J Appl Polym Sci 1995, 56, 1187.
15. Jayakrishnan, A.; Sunny, M. C. Polymer, 1996, 37, 5213.
16. Lakshmi, S.; Jayakrishnan, A. Polymer 1998, 39, 151.
17. Taverdet, J. L.; Vergnaud, J. M. Eur Polym J 1986, 22, 959.
18. Bichara, A.; Fugit, J. L.; Taverdet, J. L. J Appl Polym Sci 1999, 72, 49.
19. Crank, J. In The Mathematics of Diffusion; Clarendon Press: Oxford, 1975, 2nd ed.
20. Papaspyrides, C. D. J Appl Polym Sci 1992, 44, 1145.
21. Van Krevelen, D. W. Properties of Polymers; Elsevier: New York, 1997, third completely revised ed.
22. Polymer Handbook; Wiley-Interscience: New York, 1999, 4th ed.
23. Neogi, P. Diffusion in Polymers; Marcel Dekker, Inc.: New York, 1996.
24. Vergnaud, J. M.; Messadi, D.; Taverdet, J. L. The Quality of Foods and Beverages; Academic Press: New York, 1981, p. 113, vol. 2.
25. Kampouris, E. M. Eur Polym J 1975, 11 705.
26. Kampouris, E. M. 1975, Polymer 76, 840.
27. Papaspyrides, C. D.; Duvis, T. J Appl Polym Sci 1989, 38, 1573.
28. Papaspyrides, C. D. J Appl Polym Sci 1989, 38, 1859.
29. Riquet, A. M.; Sandray, V.; Akerman, O.; Feigenbaum, A. Sci Alim 1991, 11, 337.
30. Ducruet, V.; Riquet, A. M.; Feigenbaum, Rev. Franc. Corps Gras 1992, 11–12, 317.