Decreasing Pollution of Plasticized PVC Packaging: A Comparison of Three Plastic Treatments

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ABSTRACT: This study proposed three different treatments of plasticized PVC, which decreases diffusion of the plasticizer when the plastic is in contact with a liquid food or simulated liquid food. The treated PVCs were tested under the same operating conditions, and their efficiency was able to be assessed thanks to a diffusion model previously described. It was shown that the time and the temperature of the storage of the treated PVCs influenced the effectiveness of the treatment. © 2001 John Wiley & Sons, Inc. J Appl Polym Sci 80: 1841–1847, 2001

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

INTRODUCTION

The study of mass transfer between materials and their environment represents a very important part of basic research in physics, chemistry, and medicine. In addition, the control of such transfer and migration phenomena interests many industrial sectors, one of which is plastic packaging materials. Indeed, when these materials are used to protect, contain, and carry foods, beverages, or pharmaceuticals, the additives added to the polymer in order to improve its properties may migrate and contaminate the content. In addition, it is possible for the packed product to enter the plastic, causing embrittlement and rendering the package unserviceable. Consequently, this problem has attracted considerable legislative attention in Europe as well as in the United States.[1–5]

PVC—poly(vinyl chloride)—is a plastic very often used as packaging material (water or liquid food bottles, blood bags, etc.). But to be useful, PVC must incorporate a number of additives, such as plasticizers, heat stabilizers, antistatic agents, and lubricants, and these additives may migrate into the contents.

Plasticizers are of special importance in PVC packaging because they can reduce the processing temperature, which will avoid decomposition of the polymer and alter the processing characteristics to make the finished product softer and more flexible. In some cases, as for example with blood bags, the quantity of plasticizer can reach 40% of the plastic weight. The most important class of monomeric plasticizers is phthalate, and typical of this group is bis(2-ethylhexyl)phthalate (DEHP).[6–8]

In order to understand and solve the migration problems with PVC packaging, many researchers have studied mass transfers between plasticized PVC and various liquids. The obtained results show that in all cases there is a simultaneous transfer: the additive goes out of the PVC, and the liquid enters the plastic.[9–18]

Many parameters have a great influence on these transfers, including initial concentration of

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plasticizer, nature of the plasticizer, temperature, and nature of the liquid. The prior history of the PVC sample is also an important factor influencing the migration behavior. Therefore, if a plasticized PVC has been soaked in some liquid for a few minutes and then dried, this treated PVC's behaves very differently with respect to mass transfer. Indeed, when PVC is in contact with a liquid food or a simulated liquid food, the migration of both plasticizer and liquid is delayed, slackened, and reduced.[10,19,20] Such treatment of PVC can be used in order to avoid the migration problem in PVC packaging.

It can be conjectured that after treatment the PVC sample is like a sandwich: a slab of plasticized PVC between two membranes of PVC practically without plasticizer. Based on this hypothesis, a mathematical model able to simulate the mass transfers between liquid and plastic materials has been proposed.[21,22] The goal of this study was to compare the migration behavior of sandwich materials achieved in other ways. Therefore, we prepared a plasticized PVC slab between two PVC sheets that were practically without plasticizer. This was achieved in two ways: by assembling three slabs by compression molding and by forming two exterior PVC layers by solvent evaporation.

The comparison of the effectiveness of the three treatments (various storage conditions have been also studied) should show which is the best one for using as a packaging material and should also contribute to better understanding these additive transfers between PVC and certain liquids.

EXPERIMENTAL

Materials

Analyses of DEHP in liquid were performed by gas chromatography (Intersmat IGC 16) after the addition of diethylhexyl adipate as an internal standard. The stationary phase was Chromosorb Q and 2.5% OV 17 silicone rubber (Dow Chemical, France). Determination of the amount of DEHP released was carried out on a JASCO UV-vis apparatus at the corresponding $\gamma_{\max}$.

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 recorded by a DSC 92 Setaram.

Analysis of the DEHP in the PVC surface was performed by the IR-ATR method, as described in a previous article.[23]

Chemicals

PVC is a commercial resin (Fluka) in white powder form ($\bar{M}_n$ = 25,900 g mol^{-1} and $\bar{M}_w$ = 54,800 g mol^{-1}, T_g = 84°C). The T_g of PVC plasticized at 35% is −10°C.

Bis(2-ethylhexyl)phthalate (Prolabo), diethylhexyl adipate (Sigma), *n*-heptane (Fluka), absolute methanol (Sigma), and tetrahydrofuran (Fluka) were used as received.

Preparation of the Plasticized PVC Samples

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

The various compounds (PVC + DEHP) were pressed into sheets in a steel mold at 150°C and under a 100-bar pressure. Discs 18 mm in diameter and 0.5, 1, or 3 mm thick were cut from these PVC sheets.

Preparation of Sandwich Material

Preparation of Treated PVC by Soaking Plasticized PVC in n-Heptane

In the first stage, PVC disks were soaked in *n*-heptane for a short period of time (for example, 4 or 16 min). In the second stage, the disks were dried at 90°C for 4 min. After the treatment, the PVC was like a sandwich because the layer near the surface was practically without DEHP. In fact, analysis using an IR-ATR method[23] indicates the average concentration of DEHP to be about 7%. This type of treated PVC was labeled sample A.

Preparation of Sandwich Material by Compression Molding

Three slabs of plasticized PVC were prepared as described above: two slabs (0.5 mm) with 7% DEHP and another (3 mm) with 35% DEHP. This last sheet was placed between the two others in a steel mold, and the three samples were pressed in the mold for 12 min at a temperature of 150°C and under a pressure of 100 bar. The addition of DEHP (7 %) for the two surrounding sheets was necessary to avoid decomposition of the polymer.

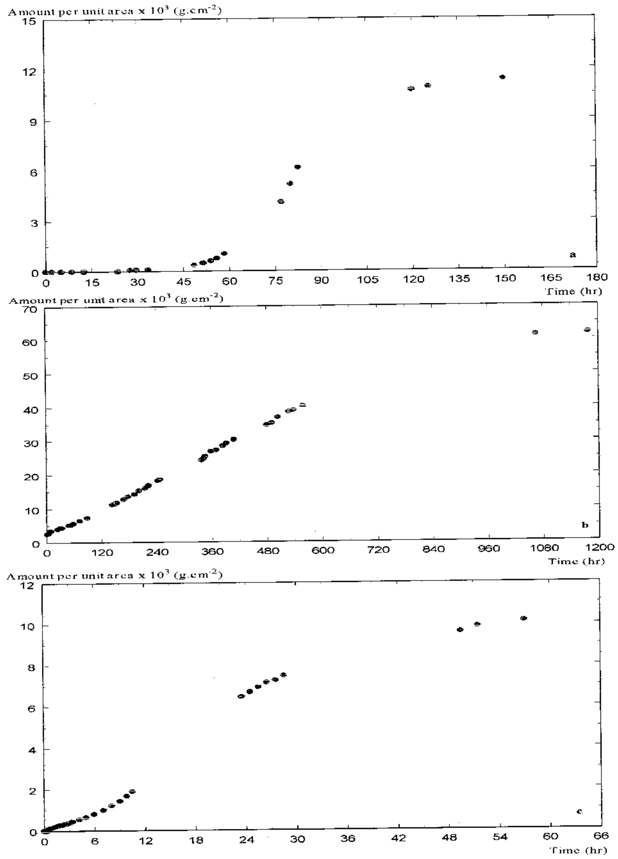

Figure 1 Migration of DEHP in n-heptane from the three treated PVCs: (a) sample A, (b) sample B, (c) sample C.

This type of treated PVC, which has a thickness of 4 mm, was labeled sample B.

Preparation of Sandwich Material by Adding a Layer of PVC

A sheet of PVC plasticized with 35% DEHP was soaked in a solution of THF with PVC (0.07 g cm^{-3}) for a short time (5 s), then dried at 90°C for 4 min. The thickness of the PVC film formed on the sheet surface during THF evaporation was determined by weighing the sheet before soaking in THF and after drying. This type of treated PVC was labeled sample C.

Test for Determining the Rate of Plasticizer and Liquid Transfer

In order to test the efficiency of the treatment dealing with mass transfers, the various PVC samples were soaked in a liquid according to these operative conditions. Diffusion experiments (labeled migration tests) were conducted in a closed flask (50 cm^3), while kept at 30 ± 0.5°C and at a controlled stirring rate. One PVC disk was immersed in 20 cm^3 of n-heptane. At various times the plasticizer was analyzed in the liquid, and the disk was weighed in order to determine the liquid quantity entering the PVC. The experiment was repeated three times, and each experiment exhibited similar results because of the good homogeneity of the plasticized PVC sheets. For the sandwich material prepared with three sheets (sample B), the edge of the PVC disk was covered with a metal ring in order to avoid the mass transfers of the disk edge.

THEORETICAL

Assumptions

In all cases studied for this article, treated PVC was defined as a sheet of PVC plasticized with 35% DEHP between two sheets of PVC that were practically without DEHP. Therefore, the model able to simulate the mass transfers between this type of material and certain liquids, described in a previous work,[21] was used in order to quantify the rate of mass transfers in terms of diffusivity.

Three diffusivities were of interest in this work:

1. The diffusion coefficient, D_0, was calculated with the approximated equation valid

Table I Results of Migration Test According to the PVC Sample, Soaking in n-Heptane without Storage

Type of Sample	Time Lag, t_d (s)	D_1 ($cm^2\ s^{-1}$)	D_2 ($cm^2\ s^{-1}$)	D_0 ($cm^2\ s^{-1}$)
Sample A	239000	1.6×10^{-11}	1.2×10^{-9}	6.0×10^{-8}
Sample B	0	—	2.1×10^{-9}	6.0×10^{-8}
Sample C	17100	3.6×10^{-10}	1.4×10^{-9}	6.0×10^{-8}

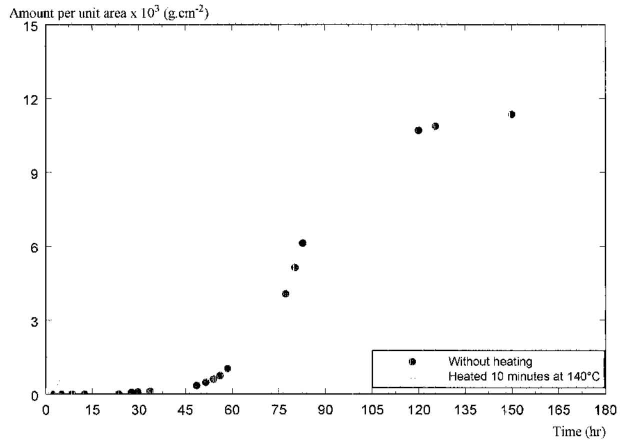

Figure 2 Influence on DEHP migration of the heating (at 140°C) of sample A before soaking in *n*-heptane.

for a slab and short times[24,25]:

$$\frac{M_t}{M_\infty} = 4.\left(\frac{D_0 t}{\Pi.e^2}\right)^{1/2} \quad (1)$$

where M_t is the amount of plasticizer (or liquid entering the disk) liberated at time *t*, M_∞ is the corresponding amount at equilibrium, and *e* is the thickness of the original disk without treatment. D_0 is the diffusivity corresponding to the initial concentration of DEHP (35%) because relationship (1) is only valid for short times, and consequently D_0 is the diffusion coefficient of the plasticized PVC without treatment.

2. The diffusion coefficient D_1 was determined by the relationship of the time-lag method:

$$t_d = \frac{\ell^2}{6.D_1} \quad (2)$$

where t_d is the time lag and ℓ the thickness of the film (one of the exterior sheets) that is practically without plasticizer. This coefficient distinguishes the diffusion rate in the membrane during the time lag. It is an average diffusivity.

3. The last value of the diffusivity is D_2, was deduced from the slope, *p*, of the straight line of the curve:

$$p = D_2 \frac{c}{\ell} \quad (3)$$

where *c* is the mass of DEHP per volume unit in the central sheet. D_2 characterizes the rate at which DEHP crosses through the membrane during the steady state.

RESULTS AND DISCUSSION

In order to test the efficiency of the various treatments of PVC, we soaked the samples in *n*-heptane at 30°C according to different storage conditions.

If the components of Figure 1(a–c) are compared, it can be observed that the three curves producing the plasticizer released from the various treated PVCs as a function of time have the same shape. This indicates that the removal of DEHP is governed by the same laws in all cases and therefore that the previously established model is valid.[21]

In addition, the value of D_2, (i.e., the diffusivity during the steady state) is about the same whatever the treatment (Table I), and the amount of DEHP released at equilibrium is always about 62% of the initial concentration. This fact does not appear clearly on Figure 1 because the amounts of DEHP released are given in absolute not relative values. Therefore, the amounts depend on the weight of the disk. For instance 12×10^{-3} g cm^{-2} [Fig. 1(a)] corresponds to about 62% of the DEHP initial concentration, and 61×10^{-3} g cm^{-2} [Fig. 1(b)] also corresponds to 62% of the DEHP initial concentration; however, in the latter case the sandwich material (sample B) is 4 times heavier than either sample A or C. For the same reason, because sample B is 4 times thicker than sample A or C, the time necessary to reach equilibrium is longer.

Therefore, whatever the treatment to which the PVC has been subjected, the removal of plasticizer is delayed and reduced. Indeed, the greater

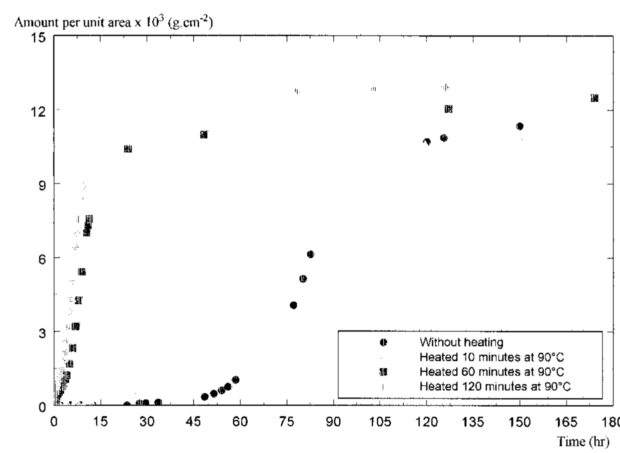

Figure 3 Influence on DEHP migration of the heating time at 90°C of sample A before soaking in *n*-heptane.

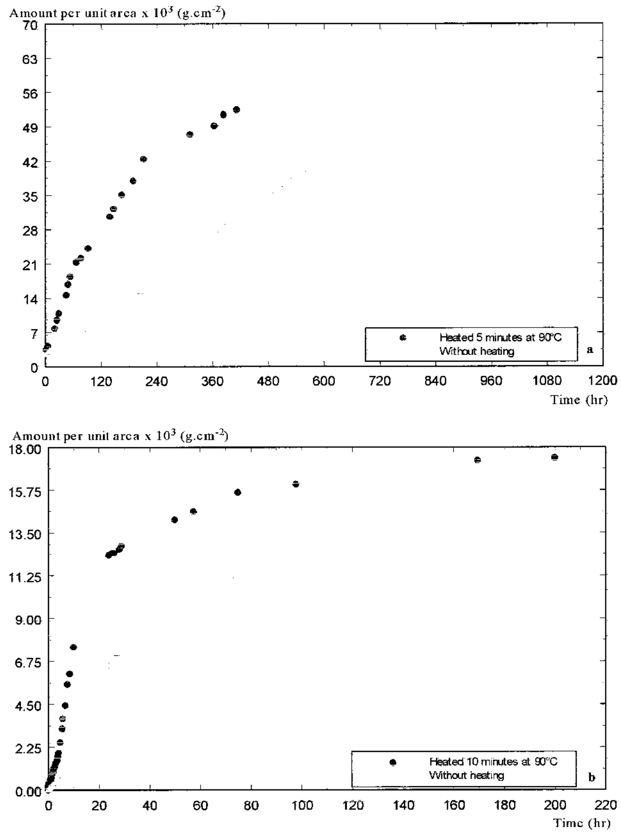

Figure 4 Effect of the temperature of storage of samples B and C on DEHP migration: (a) sample B, (b) sample C.

diffusivity (D_2) is about 1.5×10^{-9} cm^2 s^{-1}, while the diffusivity of initial PVC plasticized at 35% without treatment (D_0) is 6.0×10^{-8} cm^2 s^{-1} (Table I). Nonetheless, it should be noted that there is no time lag with the sandwich panel made only by compression molding. In order to explain this, it must be remembered that the membranes are initially plasticized with 7% DEHP. In addition, it is necessary to heat the material at a high temperature (the mold is at 150°C) in order to assemble the PVC plates.

Therefore, during this step of manufacturing the rise in temperature facilitates diffusion of the plasticizer from the region of higher concentration to that of lower concentration, that is, to the PVC "membrane." Consequently, in this case the membrane is more plasticized than the original one, and there is no time lag. In order to prove the validity of this assumption, we performed experiments as follows.

Figure 2, representing DEHP released versus time from sample A, which had been treated at 140°C for 10 min, indicates that the time lag decreases while the rate of DEHP removal increases. The results depicted in Figure 3 confirm this assumption and show that the efficiency of treatment decreases when the time of heating increases.

In order to compare the effect of the storage temperature on the various treated PVCs, we also heated samples B and C at 90°C for 5 or 10 min before testing their behavior in relation to mass transfers. In effect, the rate of DEHP diffusion increased, as can be observed in Figure 4. However, it should be noted that the diffusion coefficient D_2, which characterizes the rate at which DEHP crosses through the membrane during the steady state, does not change very much (Table II) whatever the type of sample. But with sample A the influence of the storage temperature is less important.

Finally, we tested the efficiency of the three treatments as function of the time of the storage at room temperature. Figure 5 shows the amount of DEHP released in n-heptane from the three treated PVCs stored for different times at room temperature. It can be observed that storage time has no effect on sample B. With samples A and C, only the time lag changes. Indeed, the diffusivity (D_2) maintains approximately the same value irrespective of the duration of the storage, while the time lag decreases at the same time that the period of storage increases.

Table II Results of Migration Test According to the PVC Sample as Function of Storage Temperature Conditions

Type of Sample and Storage Conditions	Time Lag, t_d (s)	D_1 (cm^2 s^{-1})	D_2 (cm^2 s^{-1})	D_0 (cm^2 s^{-1})
Sample A (90°C–10 min)	133000	3.0×10^{-11}	1.2×10^{-9}	6.0×10^{-8}
Sample A (140°C–10 min)	12400	2.6×10^{-10}	1.3×10^{-9}	6.0×10^{-8}
Sample B (90°C–5 min)	0	—	8.6×10^{-9}	6.0×10^{-8}
Sample C (90°C–10 min)	6800	6.2×10^{-10}	3.1×10^{-9}	6.0×10^{-8}

Similar results were obtained with the influx of the surrounding liquid. Indeed, the treatments have the same effects on the diffusion of n-heptane as those observed with DEHP. For example, Figure 6 shows this effect for sample A. The only difference is that the rate at which the liquid enters the PVC is always a little greater than the DEHP speed.

CONCLUSION

This work has shown that it is possible to treat a plasticized PVC in order to decrease the plasticizer migration when the plastic is in contact with a liquid food or a simulated liquid food.

Three different treatments had been proposed to reach this goal. In all cases, the contamination of the contents was slackened and reduced. When the treatment consisted of extracting plasticizer from the plastic or adding a coat of PVC on the disk surfaces, it could be observed that there was a period of time where there was no mass transfer.

However, this time lag depended on the duration and the temperature of storage. Therefore, it is advisable to use the treated PVC immediately after treatment, at least for samples A and C. In addition, whatever the treatment, it is necessary to avoid heating the treated PVCs.

The experiments described in this article agree with the model previously proposed for simulating DEHP migration in such operating conditions.

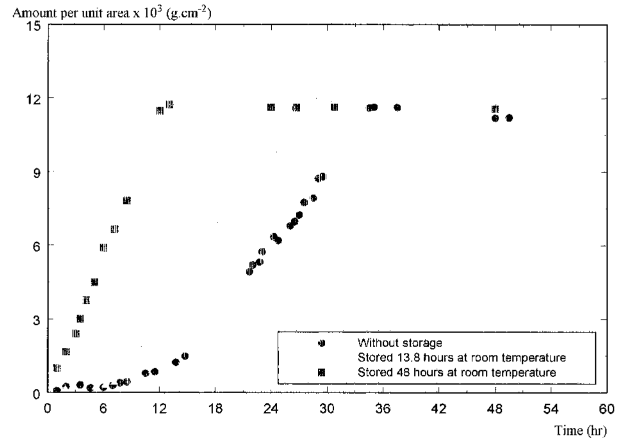

Figure 6 Effect of the time of storage (at room temperature) of sample A on n-heptane migration.

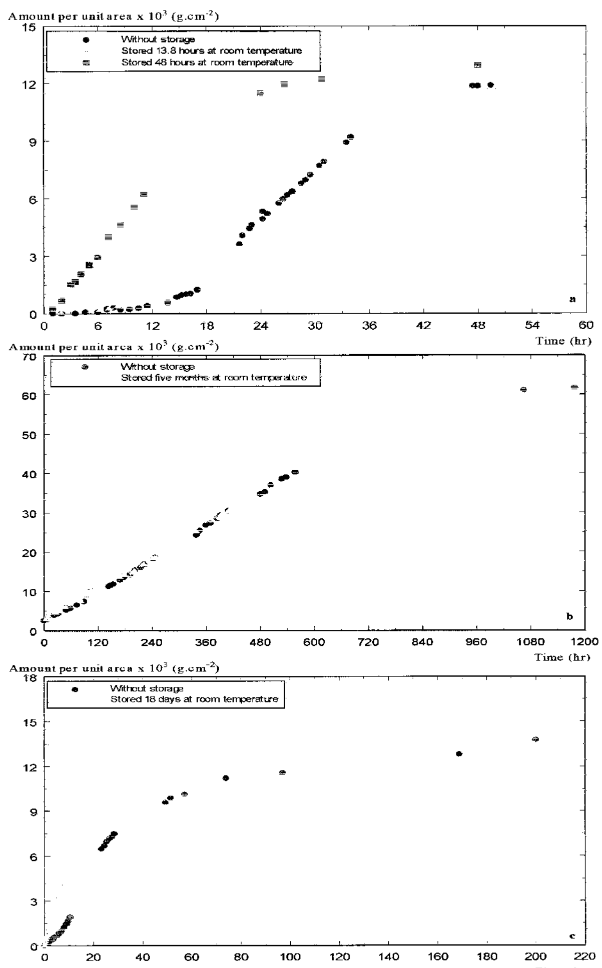

Figure 5 Effect of the time of storage (at room temperature) of samples A, B, and C on DEHP migration: (a) sample A, (b) sample B, (c) sample C.

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