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PREPARATION OF PLASTICIZED PVC COATINGS WITH LOW MATTER TRANSFERS BY USING n-PENTANE

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Abstract—When plasticized PVC is in contact with a liquid, two matter transports may take place: the liquid enters the PVC, thus enabling the plasticizer to leave. The drawbacks are thus observed, with pollution of the liquid, and alteration of the mechanical properties of the polymer. A process has been developed in order to reduce these matter transports. The two step method consists of: (i) immersing the PVC sample in a liquid for a short time, creating thus two profiles of concentrations of the liquid and plasticizer next to the surface; and (ii) evaporating the liquid which has entered the PVC during the first step. At the end of the process, a profile of plasticizer is created next to the PVC surface with a low concentration on the surface. This plasticized PVC exhibits low matter transport when immersed in a liquid, as the process is controlled by diffusion with concentration-dependent diffusivity. In the present study, a rather volatile hydrocarbon such as n-pentane is used for the first step of immersion because it is easy to remove by evaporation.

INTRODUCTION

Plasticized PVC is the leading plastic material in Europe, and it is second only to polyethylene in the United States and Japan. A large part of plasticized PVC is used in packaging for various liquids viz. food, solvents, and especially blood. When plasticized PVC is in contact with a liquid, two matter transports may take place: the liquid enters the PVC, and enables the plasticizer to leave the solid and penetrate into the external liquid, and these facts are detrimental to the purity of the liquid and mechanical properties of the solid [1, 2]. Both these transports are controlled by transient diffusion, and the problem is rather difficult for the following reasons; the diffusivities are concentration-dependent, the two transports are connected in the sense that each diffusivity depends on the concentrations of the liquid and plasticizer [3–5]. These transports are of special concern when the liquid is blood [6] as the phthalates, commonly used as plasticizers, are concentrated in various parts of the body and may be responsible for diseases.

In order to obtain flexible plasticized PVC with low matter transports, a method was developed recently [7–9]. It consists of a two-step technique:

(i) in the first step, the plasticized PVC with uniform plasticizer concentration is immersed in a liquid such as n-hexane for a given short time;
(ii) the PVC is then removed from the liquid and dried in the second step.

During the first stage of the process, two profiles of concentration are created next to the PVC surface: one with a high concentration of liquid, the other with a low concentration of plasticizer on the surface. The purpose of the second stage is to evaporate the liquid located in the PVC. As the diffusivity of the liquid is concentration-dependent and decreases with the concentrations of liquid and plasticizer, the resulting final plasticized PVC exhibits low matter transports when it is in contact again with a liquid.

In fact, the process of drying during the second stage is complex, and it is impossible to evaporate all the liquid located in the PVC. When the liquid is n-hexane, temperature as high as 120° are necessary to evaporate to dryness [10]. The process of drying is controlled not only by the evaporation from the surface but also by diffusion within the polymer. As the diffusivity of the liquid is concentration-dependent, the low value of the concentrations of plasticizer and liquid on the PVC surface is responsible for a trapping of the liquid.

The main purpose of this paper is to examine the action of another hydrocarbon which is more volatile such as n-pentane and thus easier to evaporate. The first two step process is thus achieved by immersing the plasticized PVC in n-pentane and by evaporating the liquid which has entered. A third step is considered for testing the quality of the new plasticized PVC, by immersing this new coating in n-hexane and determining the kinetics of matter transports.

THEORETICAL

Assumptions

The following assumptions are made in order to clarify the problem:

Step of absorption

(i) Two matter transports take place during this first step of absorption. The liquid enters the PVC, and the plasticizer leaves the solid.
(ii) These two matter transports are controlled by transient diffusion, with constant diffusivities.

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(iii) Equilibrium for the concentrations of liquid and plasticizer is attained on the PVC surface as soon as the process starts.

Step of desorption

(iv) The desorption of the liquid located in the PVC is controlled by diffusion within the solid and evaporation on the surface. The process of desorption is rather complex.

Mathematical treatment

The equation for the one-directional diffusion through the thickness of the sheet is:

$$\frac{\partial C}{\partial t} = \frac{\partial}{\partial x}\left(D \cdot \frac{\partial C}{\partial x}\right). \quad (1)$$

During the stage of absorption, the initial and boundary conditions are as follows:

$$t = 0 \quad -L < x < L \quad C_l = 0 \quad (2)$$

$$t > 0 \quad x = \pm L \quad C_l = C_{leq} \quad C_p = C_{peq}. \quad (3)$$

An analytical solution exists when the diffusivities are constant, and when the two matter transports are considered separately. The concentration at position x and time t is given by:

$$\frac{C_{eq} - C_{x,t}}{C_{eq} - C_{in}} = \frac{4}{\pi}\sum_{n=0}^{\infty}\frac{(-1)^n}{2n+1}\cos\frac{(2n+1)\pi x}{2L} \times \exp\left(-\frac{(2n+1)^2\pi^2}{4L^2}Dt\right) \quad (4)$$

where n is an integer

The total amount of diffusing substance which has entered the sheet (liquid) or left the sheet (plasticizer) at time $t(M_t)$ is expressed as a fraction of the corresponding quantity after infinite time (M_∞) by the relation:

$$\frac{M_\infty - M_t}{M_\infty} = \frac{8}{\pi^2}\sum_{n=0}^{\infty}\frac{1}{(2n+1)^2} \times \exp\left(-\frac{(2n+1)^2\pi^2}{4L^2}Dt\right). \quad (5)$$

For short times, when $M_t/M_\infty < 0.5$, the following equation is useful:

$$\frac{M_t}{M_\infty} = \frac{2}{L}\left(\frac{D \cdot t}{\pi}\right)^{0.5}. \quad (6)$$

EXPERIMENTAL PROCEDURES

Materials

Sheets of plasticized PVC with the following characteristics were used: thickness = 0.060 cm, square: 3 × 3 cm, % plasticizer = 30 [30 g plasticizer in 100 g PVC, 2 g additives, plasticizer: diethylhexylphthalate (DEHP)].

The liquid chosen was n-pentane for the first step of immersion. For the third step which consists of testing the behaviour of the new plasticized PVC, the PVC was immersed in n-hexane.

Apparatus for preparation and testing the PVC sample

First step of absorption. The PVC sample, square in shape (3 × 3 cm) weighing *ca* 0.6568 g was immersed in 100 ml of n-pentane at 20° in a flask with controlled stirring. After a short given time, the PVC sample was weighed and the concentration of plasticizer in the liquid determined by u.v. spectrometry (U-1100 Hitachi) at 225 mm.

Second step of desorption. The PVC sample was removed from the liquid and dried under controlled conditions of temperature and time. During the drying stage, the weight was determined at intervals.

Determination of the kinetics of transports with the non-treated PVC sample. The PVC sample was immersed in n-pentane at 20° in the same flask and same conditions of stirring. At intervals, the sample was weighed, while a small sample of liquid (0.2 ml) was taken and analysed by u.v. spectrometry.

Testing the new PVC sample. The new PVC sample, at the end of the second stage of drying, was immersed in n-hexane at 20° with the same conditions of stirring. At intervals, the sample was weighed while a small sample of liquid (0.2 ml) was analysed by u.v. spectrometry.

RESULTS

Three types of results are of interest:

(i) The determination of the kinetics of transports for the liquid and plasticizer, when the liquid is n-pentane, in order to calculate the diffusivities for these two liquids.
(ii) The preparation of the PVC sample with the first step of immersion in n-pentane, and the second step of drying.
(iii) The determination of the behaviour of the new plasticized PVC sample when in contact with n-hexane.

1. Kinetics of transports in n-pentane

The PVC sample (3 × 3 × 0.06 cm with a weight of 0.6568 g) was immersed in n-pentane (100 ml). The kinetics of the liquid absorbed by the PVC sample and of the plasticizer released by the solid were determined from the weights of the solid and concentration of plasticizer in the liquid found at intervals. These two kinetics are drawn in Fig. 1.

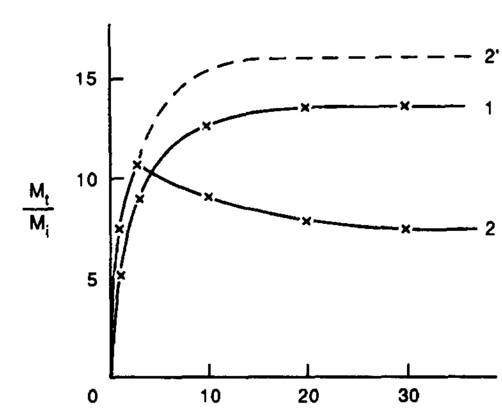

Fig. 1. Kinetics of matter transports between plasticized PVC and n-pentane. 1, Plasticizer; 2, n-pentane; 2′, n-pentane (extrapolated).

Table 1. Diffusivities and amount at equilibrium

Liquid	Diffusivity	Amount at equilibrium
n-Pentane	3×10^{-8} (cm^2/sec)	$\frac{M_\infty^l}{M_i} 100 = 16$
Plasticizer	2.7×10^{-8} (cm^2/sec)	$\frac{M_\infty^p}{M_i} 100 = 13.5$

Two conclusions are worth noting:

(i) The process of release of plasticizer is controlled by diffusion, with a vertical tangent at the beginning of the process. Equilibrium is attained after around 20 h.

(ii) The process of the absorption of liquid is far more complex as shown in earlier studies [3–5].

The liquid enters the PVC with a high rate at the beginning of the process. The amount of liquid absorbed passes through a maximum, and then decreases to the value at equilibrium.

It is easy to obtain the diffusivity from the kinetics of release of plasticizer, by plotting the amount of plasticizer released as a function of the square root of time and by using equation (6). It is far more difficult to evaluate the diffusivity for the liquid transport because of the maximum. The diffusivity is calculated by using curve 2′ obtained by extrapolation of the amount of liquid absorbed after long times. The diffusivities are shown in Table 1, as well as the amount of liquid at equilibrium.

2. Preparation of the PVC sample with low matter transports

This preparation consists of a two-step process, the first being immersion of the original PVC sample in the liquid, and the second being drying of the sample.

Stage of absorption of liquid. When the PVC sample is immersed in the liquid (n-pentane), the following two transports take place simultaneously: the liquid enters the PVC, while the plasticizer leaves the polymer. Two profiles of concentration are developed during this stage of absorption within the PVC sample. They are obtained by calculation for various time by using the data shown in Table 1 and equation (4), either for the plasticizer (Fig. 2) or for the

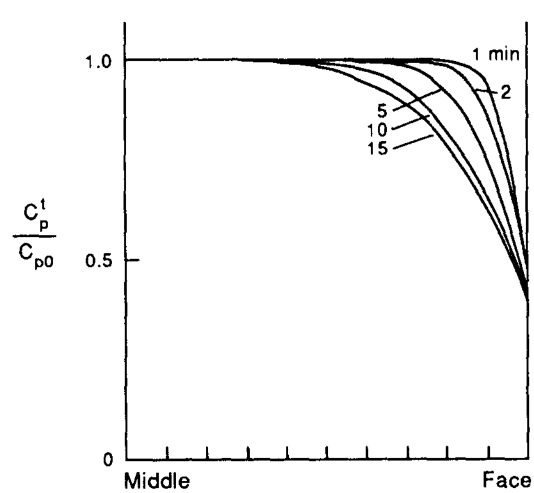

Fig. 2. Profiles of concentration of plasticizer obtained at the end of the stage of absorption.

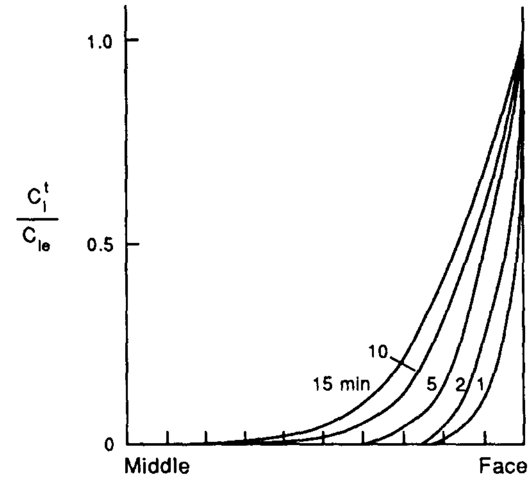

Fig. 3. Profiles of concentration of liquid (n-pentane) obtained at the end of the stage of absorption

liquid (Fig. 3). The concentrations of plasticizer and liquid on the PVC surface are calculated by considering that they are equal to the concentrations at equilibrium.

Stage of desorption of liquid. After 30 min of absorption in n-pentane (100 ml), the sample is removed and dried at 50° for 15 min. The kinetics of drying of a PVC sample ($3 \times 3 \times 0.05$ cm), previously immersed in n-pentane under the same conditions (PVC sample of $3 \times 3 \times 0.06$ cm, immersed for 30 min in 100 ml n-pentane), are shown in Fig. 4.

Some results of interest can be noted for the kinetics of drying.

(i) It is difficult to evaporate all the pentane at 50°. It takes up to 150 hr to dry the sample to completion.

(ii) Only a small part of the n-pentane is evaporated at 15 min at 50°.

(iii) The profile of concentration of the liquid is drawn in Fig. 3, at the beginning of the stage of evaporation.

(iv) The effect of the volatility of the liquid on the process of drying is of great importance. In contrast with n-hexane necessitating heating up to 120° [7] to dry completely, a temperature of 50° is high enough to achieve the process of drying with n-pentane.

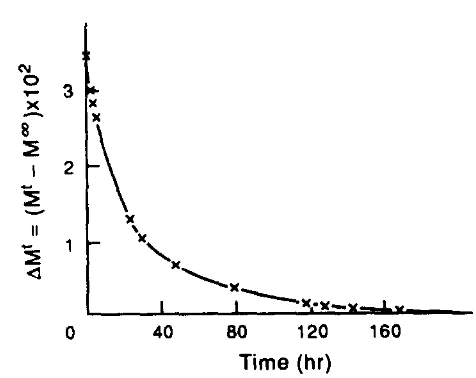

Fig. 4. Kinetics of drying at 50° of the PVC sample previously immersed in n-pentane for 30 min (second stage of the process) (g of n-pentane as a function of time in hours).

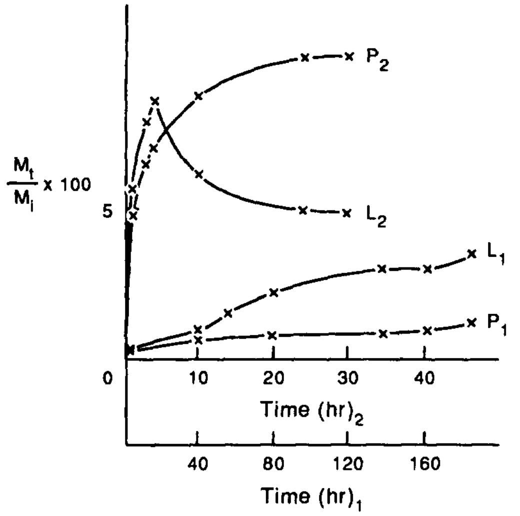

Fig. 5. Kinetics of matter transports between plasticized PVC and n-hexane. P_1 and L_1, transport of plasticizer and liquid for the treated PVC sample; P_2 and L_2, transport of plasticizer and liquid for the untreated PVC sample.

3. *Behaviour of the new plasticized PVC sample*

The new plasticized PVC sample after the two step process (absorption and drying) is tested by immersing it in n-hexane (100 ml). The PVC sample is weighed at intervals, while the concentration of plasticizer in the liquid is measured by u.v. spectrometry. From these two types of measurements, it is possible to obtain the kinetics of the plasticizer released in the liquid and of the liquid which enters the new polymer. These kinetics of liquid transports are shown in Fig. 5 for the liquid and plasticizer, for the new PVC sample and for the original PVC sample.

Some interesting conclusions can be drawn:

(i) The absorption of liquid and the release of plasticizer are considerably lower for the new PVC sample than for the original.
(ii) The transport of liquid entering the PVC is shifted to longer times with the new sample. For instance, less than 1% of liquid enters the PVC after 40 hr of immersion with the new sample, while 6% of liquid has entered the original PVC after only 1 hr.
(iii) The transport of plasticizer is considerably reduced for the new PVC sample. Only 0.9% of plasticizer is released after 150 hr of immersion with the new sample, while 8.5% is released after 10 hr with the original.

CONCLUSIONS

As shown already in previous studies, it is possible to prepare new plasticized PVC with low matter transports when in contact with a liquid.The process of preparation consists of a two stage process:

(i) immersion of the plasticized PVC sample in a liquid for a given short time at room temperature;
(ii) evaporation of the liquid which has entered the PVC during the first stage of immersion.

The nature of the liquid in which the PVC sample is immersed is of great importance, because of the difficulty in drying the PVC sample. Of course, it is easier to evaporate the liquid out of the PVC sample, when this liquid is more volatile, in spite of that fact that the process is controlled not only by evaporation but also by diffusion. The main result in this study is to show that the drying stage of the PVC sample previously immersed in n-pentane necessitates lower temperatures (around 50°) than in the case of n-hexane.

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