

Loss of plasticizers from polymer films to liquid environments: counterdiffusion aspects *versus* immersion temperature and ultra-violet-induced surface crosslinking

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Plasticized poly(vinyl chloride) (PVC) sheets were irradiated with ultra-violet light before immersion in petroleum oils to prevent plasticizer migration and counterdiffusion effects. The penetration of the liquid environment into the sheets was monitored as a function of immersion time at different irradiation levels and immersion temperatures. White spirit and kerosene penetration passes through a distinct maximum with increasing immersion time, suggesting a two-step phenomenon with liquid transfer into and out of the PVC specimens. Nevertheless, in agreement with previous experimental results on plasticizer migration behaviour, the ultra-violet treatment followed appears encouraging: the maximum penetration values do not vary significantly with irradiation time, but the equilibrium values eventually attained are positively influenced, presenting a decrease often close to 50%.

(Keywords: poly(vinyl chloride); dioctyl phthalate; petroleum oils; ultra-violet irradiation; plasticizer migration; counterdiffusion)

INTRODUCTION

Poly(vinyl chloride) (PVC) is considered one of the most important materials owing to its wide range of applications. The European PVC market is reported to have shown an 8% increase in demand in 1987, taking consumption close to 4.6 million tonnes, and the same trend was expected for 1988¹. A great percentage of these 4.6 million tonnes is consumed in the plasticized form widely used in packaging purposes.

In all applications, plasticized PVC is in contact with some kind of surrounding medium. The plasticizer may stay in place, or (more usually) it may migrate to the surrounding medium. The problem becomes very serious when packaging foodstuffs and pharmaceuticals with plasticized PVC films. These sensitive products are contaminated by the migrating plasticizer, resulting in bad taste and odour, especially after storage for prolonged periods of time². Furthermore, migration is accompanied by alteration of the mechanical properties, and the phenomenon becomes more complicated as a liquid environment in contact may migrate into the polymer sheet (counterdiffusion effects)³⁻¹⁴. The plasticizer-liquid medium mixture may gradually become a non-solvent and then separates as a second phase in the mass⁸⁻¹³. The latter phenomenon also results in alteration of the optical properties, as the PVC sheets become opaque instead of normally quasi-transparent. On the other hand, such an interaction may result in an ever-thickening layer of mixed polymer and liquid medium, and this case belongs to the general class of diffusion processes with moving boundaries^{15,16}.

In our laboratory migration phenomena have been studied for many years^{8-13,17-19}, and recently interest has been focused on preventing the problem^{10,13}. Nevertheless, as previously mentioned, any effort to reduce plasticizer migration should be related with the accompanying counterdiffusion activity. Accordingly, migration and counterdiffusion aspects in PVC/dioctyl phthalate-(DOP)/alcohol systems have been investigated for both untreated and ultra-violet (u.v.)-irradiated PVC sheets^{9,10}. Irradiation of the PVC sheets before immersion in an alcoholic environment resulted in the progressive failure of the protective surface layer of crosslinked polymer, a phenomenon attributed mainly to counterdiffusion processes¹⁰. In agreement with this observation, even at the higher doses of u.v. irradiation tested, plasticizer migration was found to be only moderately hindered.

In contrast with the above behaviour, such a failure was not observed for similarly u.v.-treated specimens tested in petroleum oils¹³. Nevertheless, the irradiation treatment followed did not result in any dramatic restriction of the migration activity for the low-viscosity media tested (kerosene and white spirit). On the contrary, the treatment proved very successful for specimens immersed in high-viscosity oils (white oil and lubricating oil).

In this paper interest is focused on the penetration activity of these petroleum oils into plasticized PVC sheets after irradiation with u.v. light to confirm some trends arising from a previous study in which only non-irradiated material was considered¹². The effects of immersion time, up to equilibrium conditions, irradiation dose and immersion temperature were examined, together with any conformity of the counterdiffusion data to elementary kinetics models. Furthermore, a

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qualitative model is proposed to correlate the total behaviour encountered with the 'structure rearrangement' mechanism¹².

EXPERIMENTAL

Reagents

The PVC was commercial grade (Esso Co., Greece), with a *k* value (a molecular-weight index for PVC polymers) equal to 70.

Immersion fluids were technical grade (Fluka AG).

Diethyl phthalate, stabilizer system, scintillation solution and also all reagents used for the synthesis of labelled diethyl phthalate were proanalysis grade (Fluka AG).

Synthesis of labelled diethyl phthalate (DOP)

Labelled phthalic anhydride (5.2 g; 7-[¹⁴C]; 1 mCi) was transferred to a reaction flask equipped with stirrer, thermometer, N₂ inlet tube, separating funnel and side condenser. The reactor was then charged with 2-ethylhexanol (211 g), phthalic anhydride (80 g) and concentrated sulphuric acid (1.5 ml). The 2-ethylhexanol was in 50% excess over the theoretical amount while toluene was also added to the reaction mixture (25% v/v based on the amount of 2-ethylhexanol). The mixture was heated under stirring in an oil bath for 2 h while the temperature was gradually raised to 170°C. During this period a slow stream of N₂ was passed and toluene was periodically added to make up for that distilling. After 2 h at 170°C, the mixture was cooled and diluted with 1 litre of ether. The ethereal solution was washed with 10% aqueous sodium carbonate solution, then with water, and finally evaporated. The diester obtained was further purified by vacuum distillation. Yield was 89% on phthalic anhydride in labelled DOP. Products with lower radioactivities were obtained by dilution with pure unlabelled DOP.

Plasticization

Suspension PVC was blended, at 80°C, with the calculated amounts of labelled plasticizer and Ba-Cd stabilizer corresponding to levels of 50 and 3 phr respectively. The dry blend was plasticized for 7 min in a Brabender Plasticorder at 170°C and 30 rpm. The plasticized mass obtained was then hot pressed to form a sheet of about 2.5 mm thickness. From this sheet, specimens of 20 × 50 mm² were cut.

Ultra-violet irradiation

Both sides of the specimens were irradiated with u.v. light (emitted mainly at 254 nm) from a 15 W GE germicidal lamp placed at a distance of 10 cm at room temperature. Gel fractions of the irradiated material were determined by extracting with tetrahydrofuran (THF) for 24 h and vacuum drying at 70°C overnight^{10,13,20,21}. The volume of solvent used for extraction was greater than 1500 ml/g of polymer.

Immersion

Each of the specimens was immersed in 250 ml liquid contained in a 300 ml glass-stoppered Erlenmeyer flask. All tests were made in duplicate and the flasks were kept in an oven fixed at three different temperatures: 37, 50 and 70°C (±1°C). To monitor weight changes the

specimens were removed from the liquid environment, wiped gently with a tissue and immediately weighed.

Radioactivity measurements

The radioactivity (R_t , counts ml⁻¹ min⁻¹) of the liquid environment is directly correlated with the amount of plasticizer that has migrated from the polymer sheet to this penetrant liquid at immersion time *t*. Divided by the radioactivity of the plasticizer employed ($R_0 = 3644.4$ counts mg⁻¹ min⁻¹) and reduced per volume of the liquid environment (250 ml), DOP migration data (M_t , mg) are provided.

The radioactivity of the liquid medium, at a given time after immersion, was measured by transferring 1.0 ml of the contents of the flask to a glass measuring vial containing 10 ml of the scintillation solution (5 g of 2,5-diphenyloxazole (PPO) and 0.3 g dimethyl-1,4-bis(5-phenyl-2-oxazolyl)benzene (dimethyl-POPOP) in 11 of toluene), shaking to ensure complete solution and measuring the radioactivity by means of a Packard 3003 Liquid Scintillation Spectrophotometer over a period of 10 min. From each flask, two samples were taken, and thus each quoted result represents the average of four measurements. Before sampling, the contents of the flasks were homogenized by swirling.

Microscopic observations

An Amplival pol-d (Jenoptic Jena GmbH) microscope was employed at a magnification range between 50 and 200.

RESULTS AND DISCUSSION

Effect of irradiation time on gel content

U.v.-induced crosslinking of PVC may result in degradation effects²⁰⁻²³. Both actions are strongly dependent on irradiation dose, i.e. irradiation time. Crosslinking results in insolubility in typical PVC solvents, while degradation becomes primarily evident by discoloration effects. Under our experimental conditions, gel content (mainly on the sheet's surface^{10,20,21}) increases linearly with irradiation time up to about 10 days and then the rate of increase declines considerably. Since beyond this limit severe discoloration of the specimen's surface was observed, irradiation time was confined to 10 days^{10,13}.

Counterdiffusion observations

The first evidence for counterdiffusion effects was based on macroscopic and microscopic observations. Independently of irradiation time the immersed specimens, initially quasi-transparent, became opaque as the liquid medium diffused into the plastic, and eventually it separated in a second phase, in agreement with previous studies^{8-13,24}. This was observed from the early stages of the immersion runs, but only when the low-viscosity oils (white spirit and kerosene) were employed. On the contrary, the high-viscosity media (white oil and lubricating oil) did not result in opacity because of limited counterdiffusion activity as mentioned below and also in ref. 12 for non-treated specimens.

Quantitative approach of the counterdiffusion process

The total amount of liquid medium that penetrated into the PVC sheet at time *t* is represented by S_t and it

can be calculated by the following equation:

$$S_t = (W_t - W_0) + M_t \quad (1)$$

where W_t and W_0 represent the weight of the specimen at immersion time t and 0, respectively, and M_t is the amount of plasticizer migrated to the liquid penetrant at the same time t .

In Figures 1-6, corresponding to the temperature and u.v. irradiation levels tested, curves of M_t versus t and S_t versus t are given for both white spirit (Figures 1-3) and kerosene (Figures 4-6). Clearly, considerable amounts of the lighter oils penetrate into the immersed specimens. On the contrary, no curves are presented for white oil and lubricating oil since the corresponding penetration

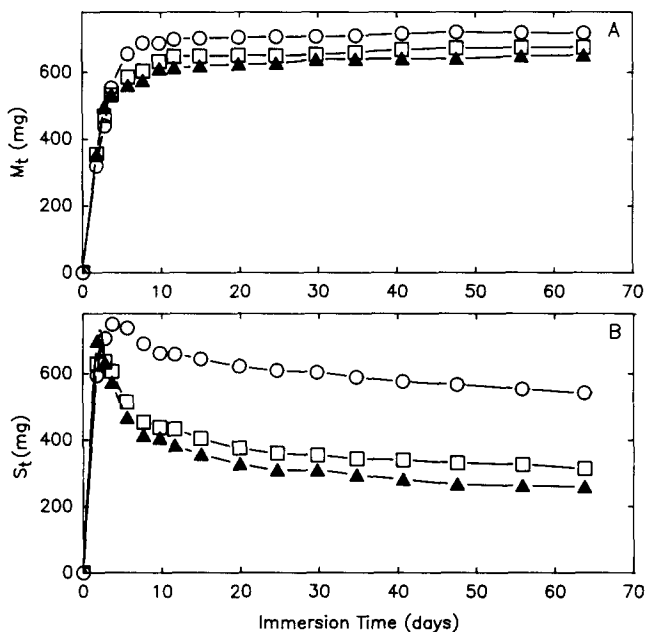


Figure 1 White spirit. Plots of plasticizer loss (A) and penetrant uptake (B) vs. immersion time at 37°C as a function of irradiation time: (○) 0 days; (□) 5 days; (▲) 10 days

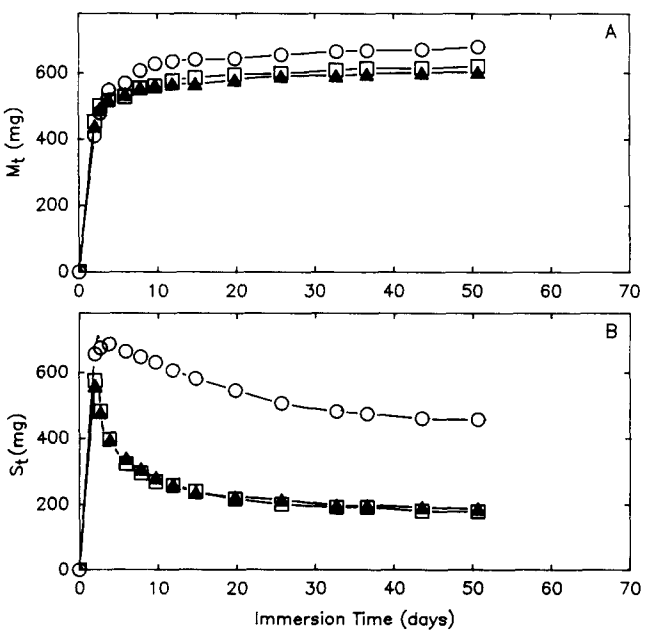


Figure 2 White spirit. Plots of plasticizer loss (A) and penetrant uptake (B) vs. immersion time at 50°C as a function of irradiation time: (○) 0 days; (□) 5 days; (▲) 10 days

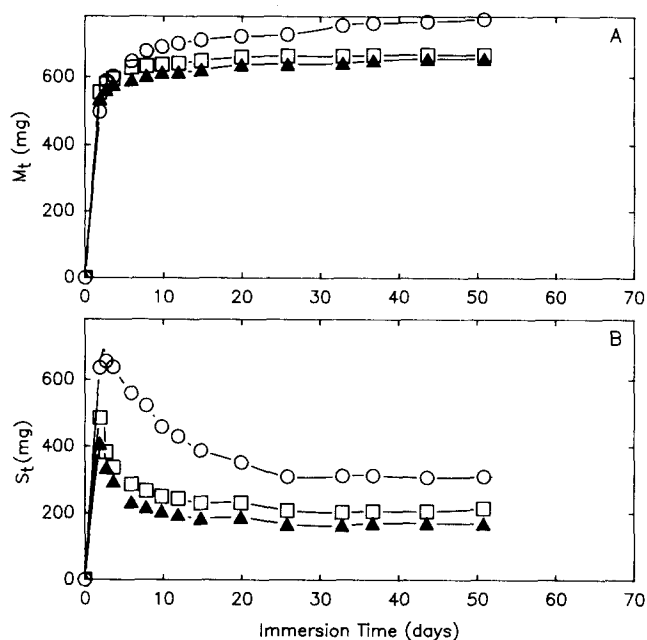


Figure 3 White spirit. Plots of plasticizer loss (A) and penetrant uptake (B) vs. immersion time at 70°C as a function of irradiation time: (○) 0 days; (□) 5 days; (▲) 10 days

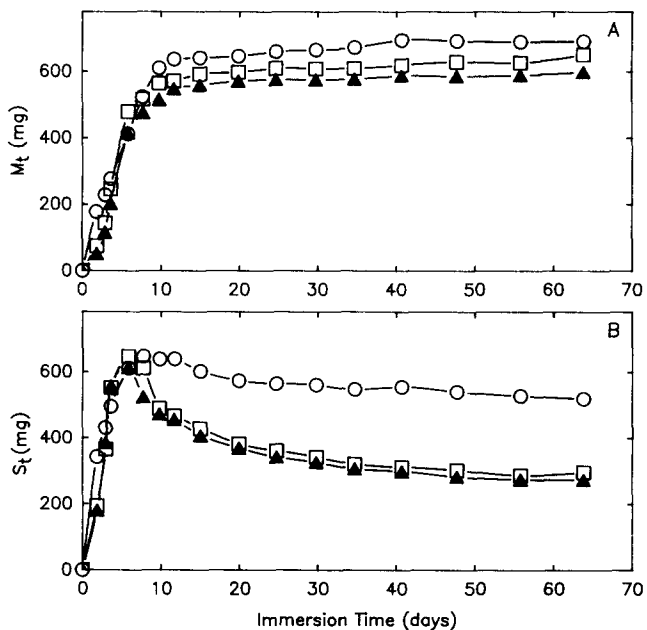


Figure 4 Kerosene. Plots of plasticizer loss (A) and penetrant uptake (B) vs. immersion time at 37°C as a function of irradiation time: (○) 0 days; (□) 5 days; (▲) 10 days

levels continuously fall near zero, in agreement with previously discussed findings for non-irradiated PVC sheets¹².

The lighter oils, independently of irradiation level, present a counterdiffusion activity very similar to that referred to in the literature for the system PVC/DOP/benzyl alcohol or ethanol-water⁵⁻⁷. The penetration curves, in all cases, are characterized by a maximum appearing at the initial stages of the total process. In other words, the amount of white spirit or kerosene transferred into PVC increases at the beginning of immersion, rises to a maximum value and then decreases until equilibrium. Thus, the counterdiffusion process comprises a two-step phenomenon with liquid transfer into and out of the PVC

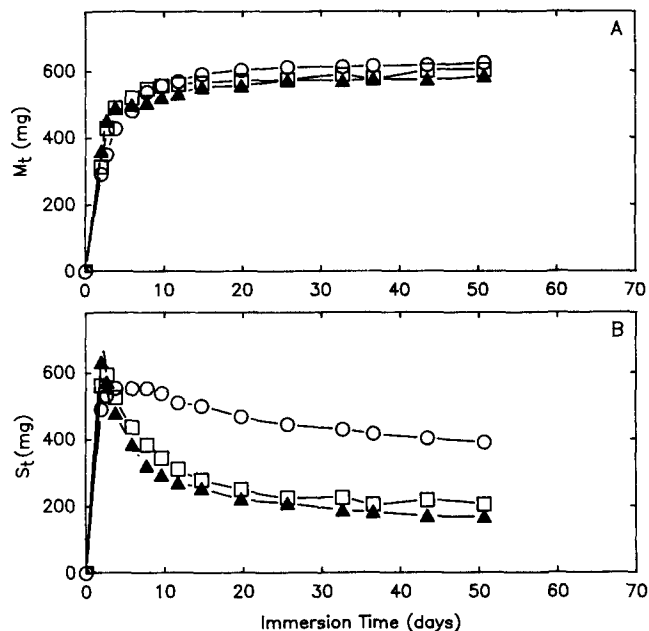


Figure 5 Kerosene. Plots of plasticizer loss (A) and penetrant uptake (B) vs. immersion time at 50°C as a function of irradiation time: (○) 0 days; (□) 5 days; (▲) 10 days

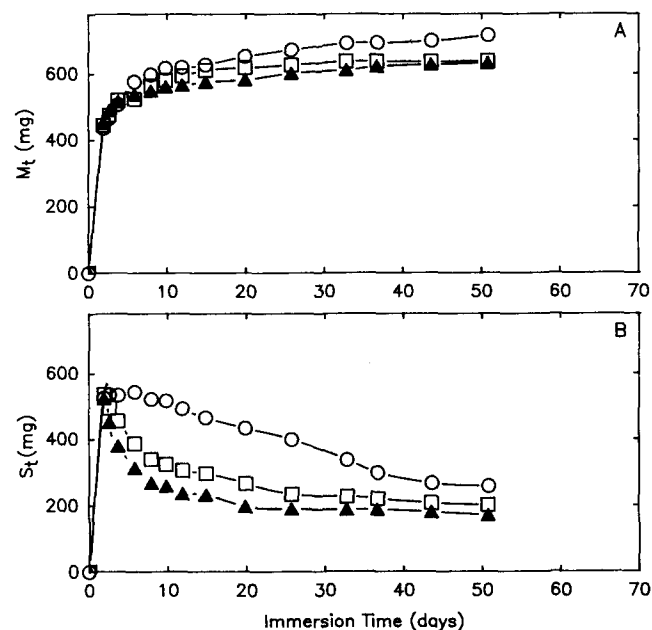


Figure 6 Kerosene. Plots of plasticizer loss (A) and penetrant uptake (B) vs. immersion time at 70°C as a function of irradiation time: (○) 0 days; (□) 5 days; (▲) 10 days

sheets. On the other hand, since the appearance of a maximum in the S_t versus t curves substantially coincides when high migration rates are obtained, considerable swelling of the specimens did not happen. It should be emphasized here that there is a direct correlation between the penetration ability of a liquid medium into plastics and the migration of low-molecular-weight components into this liquid⁴. On the other hand, white oil and lubricating oil do not penetrate, and the migration is similarly very limited^{11,13}.

The behaviour reflected from Figures 1B-6B is in agreement with the results for the untreated specimens, discussed also in ref. 12. However, in the latter case the pattern of the aforementioned peaks is wide, in contrast with the treated specimens, where the peaks are narrow and possibly appear at earlier immersion times.

Based on the data quoted in Figures 1B-6B, in Table 1 are tabulated maximum values of the amount of liquid counterdiffused, expressed on an initial weight basis, and also the equilibrium values attained, similarly reduced. The following remarks can be made.

Counterdiffusion at maximum. As temperature increases, penetration at maximum for both white spirit and kerosene is restricted to lower values for all irradiation levels. On the other hand, penetration at maximum is not influenced systematically when irradiation time increases at constant immersion temperature. Nevertheless, it should be mentioned that since the maxima appear very early it can be assumed that the real maximum data are lost. Within the 50 or 60 days time span of immersion, the first samples were taken 40-45 h after initial immersion and therefore it cannot be excluded that higher maximum values appeared within this period of time.

Counterdiffusion at equilibrium. Important differences exist in the results of u.v. irradiation on equilibrium or quasi-equilibrium counterdiffusion, as the respective values for the treated specimens are much lower than those for the untreated ones (Table 1, Figures 1B-6B). Accordingly, the u.v. treatment is satisfactorily effective in reducing the extent of the penetration eventually attained, in contrast with results on migration. In the latter case, as also shown in Figures 1A-6A, the prevention effect is small¹³. Furthermore, it is worth while to remark that small differences in counterdiffusion at equilibrium arise, for both media, when irradiation time increases from 5 to 10 days, and this often seems

Table 1 Maximum and equilibrium (or quasi-equilibrium) values of liquid counterdiffused as a function of immersion temperature and irradiation time^a in two liquid environments

Immersion temperature (°C)		Irradiation time (days)					
		White spirit			Kerosene		
		0	5	10	0	5	10
37	max.	24.6	20.8	23.3	21.7	21.9	21.6
	equil.	17.8	10.3	8.7	17.4	10.0	9.6
50	max.	22.2	19.1	19.0	18.9	19.5	21.3
	equil.	16.1	7.3	6.4	13.3	6.7	5.7
70	max.	21.9	16.5	14.2	18.4	17.9	17.6
	equil.	10.4	5.9	5.9	7.0	6.7	5.7

^a All quoted values are expressed on initial weight percentage basis¹²

to be the case for the plasticizer migration data. On the other hand, the influence of immersion temperature is the same as that met for the maximum values: as temperature increases, penetration at equilibrium for both white spirit and kerosene decreases for all irradiation levels.

White spirit versus kerosene. An interesting observation can be made when considering the differences in counterdiffusion between white spirit and kerosene. Under exactly the same experimental conditions, the untreated specimens immersed in white spirit presented higher maximum values and also higher equilibrium or quasi-equilibrium values. This is not always true after irradiation.

Migration and counterdiffusion elementary kinetics

Theoretical. Transport processes fall into 'Fickian' and 'non-Fickian' categories. Depending on the relative rates of penetrant mobility and polymer segment relaxations, case I (Fickian) and case II are viewed as the two limiting types of transport processes^{25,26}.

The usual assumptions for the treatment of diffusion behaviour may not be applicable in solid-liquid plasticizer migration and counterdiffusion owing to the possibility of occurrence of state transitions during the diffusion process. This becomes especially important when these diffusional exchanges occur near the glass transition temperature of the polymer system⁹. In fact, when great rates of plasticizer migration are initially encountered, so that nearly all the plasticizer contained is transferred into the surrounding liquid, the glass transition temperature decreases and deviation from Fickian kinetics is expected. On the other hand, no considerable plasticization effect should be expected from the liquid medium penetrated if separation of the latter into a second phase occurs. Accordingly, a great amount of research has been oriented to establishing and solving the corresponding implications of the diffusion mathematics due to the complexity of the total behaviour, but the general applicability of some of the models proposed remains limited²⁴. Nevertheless, simple migration models are often proposed, based on Fick's law with constant diffusion coefficients, simple boundary conditions, negligible relaxation effects and constant polymer volume^{24,27-29}. Thus, in accordance with previous studies^{5-7,9-13} on migration phenomena, the following well known Fickian approximation for short times is used:

$$MS_t/MS_\infty = 2(Dt/\pi l^2)^{1/2} \quad (2)$$

where MS_t denotes the total amount diffused (of plasticizer migrated or liquid counterdiffused) at time t , MS_∞ the corresponding quantity after infinite time and D the diffusion coefficient, while the PVC specimens are considered as plane sheets having a thickness $2l$.

A plot of MS_t/MS_∞ against $2(t/\pi l^2)^{1/2}$ is initially linear and provides the diffusion coefficient for the early stages of the diffusion process.

The exact derivation of equation (2) together with a thorough discussion on all the assumptions required has been given elsewhere⁹⁻¹¹.

Results. In accordance with previous studies^{5-7,9-13}, and taking into account the absence of swelling, i.e. good dimensional stability, the short-times approximation of the one-dimensional Fick's diffusion equation (equation

(2)) can be a good basis for trying to fit our experimental data. On the other hand, since no considerable differences arise between 5 and 10 days irradiation time (*Figures 1B-6B* and *Table 1*) the analysis has been restricted to the reference samples (non-treated) and those irradiated for 5 days.

As already mentioned, the counterdiffusion process appears to be a two-step phenomenon, i.e. consisting of a sorption step up to a certain point, followed by a desorption step. Both steps were considered separately and the validity of equation (2) was tested under the following assumptions^{6,12}. The maximum amount of liquid sorbed has been considered as an equilibrium amount. On the other hand, for the desorption step, the same amount was assumed to be initially contained in the sheet while the time of its appearance has been defined as the starting time ($t=0$) of the desorption process. Of course, the possible error in determining exactly the position of the peak, i.e. the transition from sorption to desorption, should be emphasized again here.

In terms of a penetrant activity-concentration relationship³⁰ it is necessary to assume that the total process consists of three stages:

(i) Initial penetration into the polymer, where the activity-concentration relationship is constant with time t (sorption stage).

(ii) 'Instantaneous' loss of plasticizer, which increases the activity of the penetrant in the polymer. This seems valid because of the observed coincidence of the penetrant sorption peaks with the range of increased migration rate (*Figures 1-6*).

(iii) Subsequent loss of the penetrant sorbed as it approaches the new equilibrium (desorption stage). This stage is characterized by decreased plasticizer levels into the polymer and decreased activity gradient due to the restriction of the system's mobility.

In *Figures 7* and *8*, corresponding to a temperature of 37°C, the conformity of the sorption (A) and desorption data (B), at the initial stages, to equation (2) can be seen for white spirit (*Figure 7*) and kerosene (*Figure 8*). Except for the non-treated specimens during sorption (correlation coefficient $r^2 = 1.00$) the fitting is not satisfactory ($r^2 = 0.64$

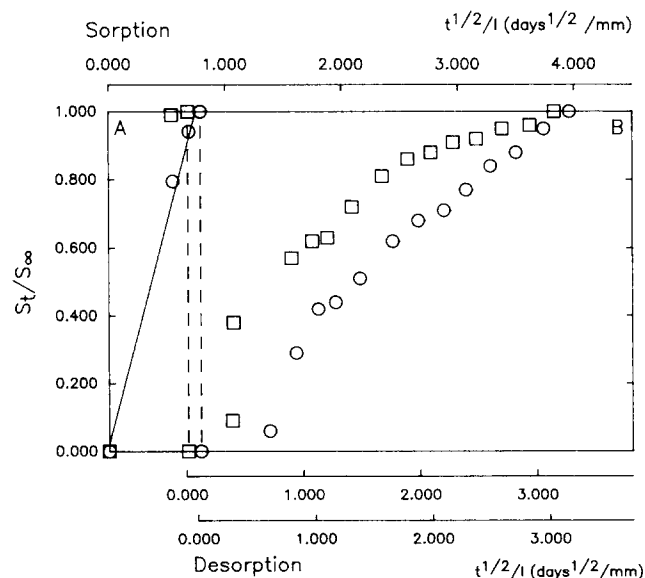


Figure 7 White spirit: Fickian (short-term) correlation of counterdiffusion data at 37°C for the sorption (A) and desorption (B) stages: (○) non-treated PVC; (□) u.v.-irradiated PVC (5 days)

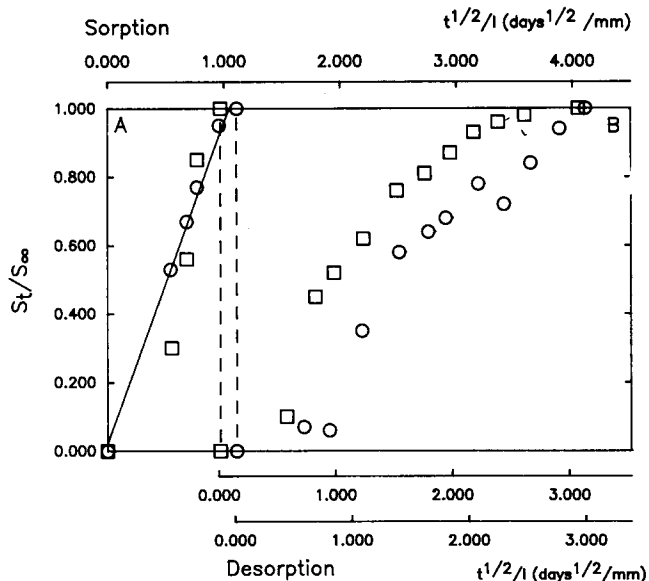


Figure 8 Kerosene. Fickian (short-term) correlation of counterdiffusion data at 37°C for the sorption (A) and desorption (B) stages: (○) non-treated PVC; (□) u.v.-irradiated PVC (5 days)

to 0.93). The picture is typical and rarely changes at higher temperatures of 50 and 70°C. Furthermore, for the sorption stage, even at 37°C, it was realized that the data available are not sufficient for a reliable test of conformity to Fick's law (Figures 1–6). This was due to the fact, referred to above, that the maximum value is attained early, and in future work more experimental points at the very initial stages should be collected. Therefore, kinetics studies for the sorption process at 50 and 70°C cannot be carried out with reliability.

In spite of the above results, Figures 7 and 8 are useful for evaluating counterdiffusion differences between white spirit and kerosene, and also the u.v. treatment effect. At 37°C, in white spirit, the polymer seems more permeable in either sorption or desorption. On the other hand, no resistance to counterdiffusion is effected due to the u.v. irradiation. On the contrary, sorption and especially desorption cycles are accelerated.

Qualitative model

A possible mechanism fitting the behaviour of the untreated specimens was proposed in a previous paper¹². Two points were then discussed.

(i) As the plasticizer migrates to the surrounding liquid, the system gradually turns to nearly non-rubbery behaviour, in agreement with macroscopic observations. On the other hand, no considerable plasticization effect should be expected from the liquid medium penetrated owing to the evident separation into a second phase. Accordingly, no conformity also to long-term Fickian expressions with constant diffusion coefficient should be expected²⁵. Our data (from either irradiated or non-irradiated specimens) confirm this supposition, as the correlation coefficient did not exceed the level of 0.93.

(ii) Commercial PVC is supposed to be a typical semicrystalline polymer, although it has been proposed that a portion of the apparently crystalline material is in a mesomorphic condition with only two-dimensional order^{31–33}. In any case, the effect of keeping the immersed material at the elevated temperatures considered for very

long times cannot be neglected. In other words, rearrangement of the structure to a more ordered and compact scheme may take place during immersion. The term 'annealing' may also be used and, if it is real, comprises another transition state encountered during the total process. Nevertheless, such an assumption is well supported by the plasticizer migration data^{11,13,34}. As immersion temperature increases, long-term or equilibrium plasticizer migration values pass through a minimum. In other words, the extent of annealing increases, but at the highest temperature tested the effect of immersion temperature becomes more pronounced, so that plasticizer migration increases again^{11–13}. On the other hand, counterdiffusion also fits well the rearrangement model proposed above. In fact, even if the remaining plasticizer–oil mixture does not result in restoring plasticization of the material, due also to the sorption–desorption process, its presence may still contribute to some mobility at the molecular level favouring structural rearrangement¹².

Turning back to the data of this study, the annealing hypothesis may also be correlated with the equilibrium counterdiffusion activity when immersion temperature or irradiation time increases (Table 1).

Effect of immersion temperature at constant irradiation level. For each irradiation level, when the temperature increases the desorption rate rises, so that a lower counterdiffusion level is established at equilibrium. Accordingly, it should be accepted that here the effect of the annealing process is not important due to molecular size differences. The mobility of the petroleum oils of smaller molecular volume is not affected compared with the plasticizer molecules for which the influence of structural rearrangement in their diffusional behaviour is significant.

Effect of u.v. irradiation level at constant immersion temperature. When considering the effect of irradiation, at a given temperature level, the following mechanism can be proposed: desorption rate increases with irradiation time (also Figures 7B and 8B) because the extent of the corresponding annealing declines, at this temperature level. Such a statement can be supported by the supposition that, within the core of the PVC sheet, the structural rearrangement remains the same, but this is not the case at the crosslinked surface layer, characterized by limited structural mobility. The latter is less susceptible to structural rearrangement and therefore its existence now contributes less to preventing liquid desorption. In other words, owing to the u.v. treatment, the loss of plasticizer from the surface does not lead to such great relaxation of the glass, which hence has lower barrier properties. Furthermore, the crosslinked layer is to some extent capable of preventing the bulkier plasticizer molecules from escaping out of the sheet (Figures 1A–6A) but not restricting the mobility of the counterdiffused molecules. The following experimental fact also supports this mechanism. The peaks at maximum counterdiffusion, in the very early stages of the process, are often insensitive to u.v. irradiation (Table 1).

The above explanations are also compatible with the broad peaks detected for the untreated specimens of the S_t versus t curves (Figures 1B–6B). The more compact structure reduces the desorption rate of the liquid counterdiffused. On the contrary, after irradiation for 5 or 10

days these maxima are very distinct. Finally, in view of the assumptions of infinite baths and negligible boundary effects^{11,13}, the aforementioned rearrangement-annealing model is compatible with the observation that not all the liquid sorbed (and also the plasticizer contained^{11,13}) is removed from the PVC specimens even after immersion for 50 to 65 days.

CONCLUSIONS

White spirit and kerosene penetration passes through a distinct maximum with increasing immersion time, suggesting a liquid transfer into and out of the PVC specimens.

In general, penetration behaviour, either sorption or desorption, is characterized by limited conformity even to simple expressions such as Fick's law.

As immersion temperature increases, penetration at maximum for both white spirit and kerosene is restricted to lower values for all irradiation levels. On the other hand, penetration at maximum is not influenced systematically when irradiation time increases at constant immersion temperature.

The u.v. treatment tested is satisfactory in reducing the extent of the penetration eventually attained, at equilibrium, in contrast with the corresponding results on migration.

Keeping the specimens at elevated temperatures in the liquid media considered for very long times may result in 'annealing', i.e. the three-component structure (non-crosslinked polymer/plasticizer/liquid) may rearrange itself to a more compact scheme. Furthermore, it seems worth while to assume that differentiation exists in this annealing behaviour between surface and core of the plastic sheet due to u.v. treatment effects.

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