Plasticized PVC Films/Petroleum Oils: The Effect of Ultraviolet Irradiation on Plasticizer Migration

T. DUVIS, G. KARLES, and C. D. PAPASPYRIDES*

Laboratory of Special Chemical Technology, Department of Chemical Engineering, National Technical University of Athens, Athens 106 82, Greece

SYNOPSIS

Plasticizer migration from flexible poly(vinyl chloride) comprises an important aspect, especially when packaging foodstuffs and pharmaceuticals. Much of the published work has been intended either to correlate migration into simulants with that into foods or to study migration into simpler extractants, enabling the various parameters involved in migration to be studied in isolation. According to the latter approach, the migration of dioctyl phthalate into petroleum oils has been studied already in our laboratory and in this paper results are presented in an attempt to reduce or prevent migration by u.v. irradiation. The effect of irradiation time on short- and long-term migration behavior was examined together with the influence of the immersion temperature. The nature of the liquid environment seemed to be a predominant aspect: high viscosity oils presented a satisfactory behavior in contrast with those of lower viscosity in which the prevention effect was rather negligible. On the other hand, primary kinetics studies yielded similar results with those already established for untreated material (i.e., good conformity to the short time Fickian approximation).

INTRODUCTION

Poly(vinyl chloride) (PVC) comprises one of the most widely used polymeric materials. Due to the high consumption of this polymer in the flexible form the critical problem remains: plasticizer, but also other additives migrate from the plastic to the surrounding media. The mechanical behavior changes and the environment in contact is contaminated. The problem becomes very serious in packaging foodstuffs and pharmaceuticals and this explains why a considerable volume of legislation has been developed in the EEC, United States, and elsewhere.[1]

Many factors can influence the additives and monomer residues migration: temperature, compatibility of the migrant with the polymer, molecular size of the migrant, compatibility of the migrant with the phase external to the polymer, and counterdiffusion phenomena (i.e., interactions that may occur between the external phase and the polymer).[1–18]

The migrating plasticizer can be determined either as the amount leaving the polymer or the amount entering the liquid. A wide variety of experimental methods have been used, including weight loss,[2–5] chromatography,[6,7] spectroscopy,[8,9] and radio-activity.[2–5,10–15]

Turning to efforts on reducing or completely preventing migration simple techniques include placing paper or metal foil on the surface of plasticized PVC film,[19,20] or coating with polyurethanes,[21–23] polyacrylates,[24–26] polyesters,[22,27] and polyamides.[28,29] Furthermore, it has been attempted to modify the structure of the material itself by either crosslinking or incorporation of bulky substituents (i.e., to restrain the mobility of the system species).[10]

Crosslinking may be induced chemically (i.e., by processing with peroxides)[30] or by radiation in the presence[31] or absence of multifunctional monomers. In the latter case, use of gamma rays,[32] u.v. light[13,33–35] and plasma treatment[36–40] has been widely applied for preventing migration.

In our laboratory migration phenomena have

been extensively studied[2-5,12-15] and recently the interest is focused also on preventing the problem. In particular, migration aspects in PVC/dioctyl phthalate (DOP)/alcohol systems have been investigated for both untreated and u.v. irradiated PVC sheets[12,13]: Within our experimental conditions, migration was found to be only moderately hindered due to the progressive failure of the protective surface layer developed during radiation treatment. On the other hand, all migration data collected were tested against typical kinetics models to reveal conformity to the Fickian approximation for short times, for both untreated and u.v. treated specimens.

In this paper suspension PVC was plasticized with labelled DOP and specimens made were irradiated by u.v. light for several days. Afterwards, the specimens were immersed for long periods in petroleum oils, namely white spirit, kerosene, white oil, and lubricating oil. The effect of irradiation time on migration behavior was examined together with the influence of the immersion temperature. The nature of the liquid environment seemed to be a predominant aspect while any conformity to simple kinetics models was also examined.

EXPERIMENTAL

Reagents

PVC: Commercial grade, Esso Co., Greece, with a k value (a molecular weight index for PVC polymers) equal to 70.

Immersion fluids: Technical grade, Fluka AG.

Dioctyl phthalate, stabilizer system, scintillation solution and also all reagents used for the synthesis of labelled dioctyl phthalate: Proanalysis grade, Fluka AG.

Synthesis of Labelled Dioctyl Phthalate (DOP)

Labelled phthalic anhydride (5.2 g; 7-^{14}C; 1 mCi) was transferred to a reaction flask equipped with stirrer, thermometer, N_2 inlet tube, separating funnel, and a side condenser. The reactor was then charged with 2-ethyl hexanol (211 g), phthalic anhydride (80 g), and concentrated sulfuric acid (1.5 mL). The 2-ethyl hexanol was in 50% excess over the theoretical while toluene was also added to the reaction mixture (25% v/v based on the amount of 2-ethyl hexanol). 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 N_2 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 L 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, 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 the levels of 50 and 3 phr, respectively. The dry blend was plasticized for 7 min in a Brabender Plasticorder at 170°C and 30 200r.p.m. 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 mm were cut.

Ultraviolet Irradiation

Both sides of the specimens were irradiated with UV light (emitted mainly at 254 nm) from a 15W 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.[13,41] 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 glass-stoppered Erlenmeyer flask of 300 mL. All tests were made in duplicate and the flasks were kept in an oven fixed at three different temperature levels: 37, 50, and 70°C (±1°C).

Radioactivity Measurements

The radioactivity (R_t, counts per mL per min) of the liquid medium is directly correlated with the amount of the plasticizer migrated at immersion time t. Divided by the radioactivity of the plasticizer employed (R_0 = 3644.4 counts per mg per min) and reduced per liter of the liquid environment, DOP concentration data (in mg/L or g/L) 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 flasks to a glass mea-

suring vial containing 10 mL of the scintillation solution (5 g of PPO and 0.3 g dimethyl-POPOP in 1 L 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 thus each quoted result represents the average of four measurements. Before sampling, the contents of the flasks were homogenized by swirling.

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.[42,43] Migration can be faced as a typical desorption process, and any attempt to construct a model has to be considered under these elementary principles.

Diffusion of low molecular weight substances in and out of a polymer occurs mainly in the amorphous phase. The mechanism changes character for the polymer in the glassy state below the glass transition region or in the rubbery state above the glass transition region. Certain cases of the diffusion in the glassy state have been described by Case II behavior, in which diffusion is rapid in comparison with the slow relaxation process of the polymer network in this state.[43] On the contrary, in the rubbery state the diffusion phenomenon is generally conforming to Fick's law describing the flux of the diffusing species per unit area as a function of its concentration gradient.

Plasticizer migration from the PVC material to the surrounding liquid medium comprises a three-step process:

1. Plasticizer transfer in the PVC itself by internal diffusion.
2. Plasticizer transfer through the PVC-liquid interface from the solid into the liquid.
3. Diffusion of plasticizer in the liquid.

Steps (2) and (3) are quite dependent on stirring and plasticizer-liquid compatibility.[44]

Usual assumptions for the treatment of diffusion behavior may not be applicable in the case of solid/liquid plasticizer migration due to the possibility of occurrence of state transitions during the diffusion process. This becomes especially important when this diffusional release occurs near the glass tran-

sition temperature of the polymer system.[12] 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. Nevertheless, in many cases, simple migration models have been proposed, based on Fick's law with constant diffusion coefficients, simple boundary conditions, negligible relaxation effects, and constant polymer volume.[45] Thus, in agreement with previous studies[7,12-15,46] the following assumptions are initially made:

1. The PVC specimens were considered as plane sheets having a thickness 2 L. The plane sheets were so thin that all the diffusing substance effectively entered through the plane faces and a negligible amount through the edges. Dimensional stability was further assumed.[15,47]

2. The process was treated as a nonsteady phenomenon and the transfer was described by Fick's law expressed in one dimension, with a nonconcentration dependent diffusion coefficient.

3. The volume of the liquid was supposed infinite. Actually this is a realistic assumption as only one specimen was immersed in 250 mL of liquid while usual migration procedures, as referred in the literature, involve up to 20 specimens in 200 mL of liquid.[7,46] Furthermore, boundary layer phenomena were ignored for two reasons[14]: (a) Compatibility between DOP and petroleum oils is acceptable especially for the low viscosity mediums,[2] (b) no stirring was applied, but before taking samples thorough swirling of the flask contents was carried out. This procedure has been applied in all migration studies in our laboratory.[2-5,12-15] Furthermore, it is known that boundary phenomena, when exist influence the very initial stages of the migration process.[7,46,48]

Under the above considerations elementary diffusion mathematics can be described as follows[42]: The diffusion equation in one dimension is reduced to

$$\partial Q/\partial t = D(\partial^2 Q/\partial x^2) \qquad (1)$$

where D is the diffusion coefficient taken as non-concentration dependent, Q is the plasticizer concentration at time t, and x is the coordinate dimension in the direction of the transport.
The initial conditions are

$$t = 0, \quad -L < x < L, \quad Q = Q_0 \quad \text{sheet space}$$

$$Q = 0 \quad \text{liquid space}$$

and the boundary conditions are

$$t > 0, \quad x = \pm L, \quad Q_1 = 0 \text{ (PVC face)}.$$

In other words, on the PVC faces, the rate at which plasticizer enters the liquid is always equal to that at which it leaves the PVC.

The solution of the eq. (1) is given in the form of a trigonometric series, for the plasticizer concentration in the PVC space. Since Q_1 equals zero the solution becomes

$$1 - \{(Q - Q_0)/(Q_1 - Q_0)\} = Q/Q_0 =$$

$$= \frac{4}{\pi} \sum_{n=0}^{\infty} \frac{(-1)^n}{2n+1} \exp[-D(2n+1)^2\pi^2 t/4 L^2]$$

$$\times \cos \frac{(2n+1)\pi x}{2 L}. \quad (2)$$

If M_t denotes the total amount of plasticizer desorbed at time t, and M_∞ the corresponding quantity after infinite time, then

$$M_t/M_\infty = 1 - (8/\pi^2) \sum_{n=0}^{\infty} \frac{1}{(2n+1)^2}$$

$$\times \exp[-D(2n+1)^2\pi^2 t/4 1^2]. \quad (3)$$

Equation (3) can be well approximated by the following

$$M_t/M_\infty = 1 - (8/\pi^2)\exp(-D\pi^2 t/4 1^2) \quad (4)$$

while the corresponding approximation for small times is

$$M_t/M_\infty = 2(Dt/\pi 1^2)^{1/2}. \quad (5)$$

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

RESULTS AND DISCUSSION

Effect of Irradiation Time on Gel Content

It is well known that degradation effects occur simultaneously with crosslinking when irradiating PVC by u.v. light.[41,49,50] Both actions are strongly depended on irradiation dose (i.e., irradiation time). Crosslinking results in insolubility in typical PVC solvents while degradation becomes primarily evident by discoloration effects. Accordingly, it seemed
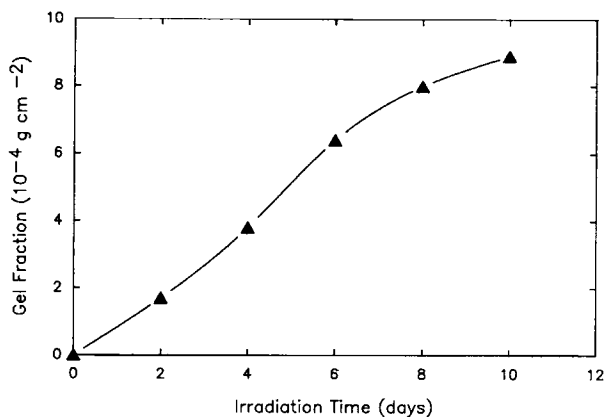

Figure 1 Relationship between gel content and irradiation time.

worthwhile to define an optimum irradiation time in terms of degradation[13]: Specimens were irradiated for different time intervals and the results after extraction with THF are shown in Figure 1. The gel content (i.e., crosslinked material), increases steadily with irradiation time up to 8 to 10 days when the curve seems to become concave to the abscissa. Thus, in order to restrain degradation it was decided to confine irradiation time up to 10 days.

Migration Behavior of Irradiated Material

The results are presented in two different groups depending on medium viscosity. Always, for each temperature level considered, migration data are given as a function of irradiation time (0, 5, and 10 days).

Low Viscosity Media

White Spirit

In Figures 2A, 3A, and 4A, corresponding to the three temperature levels tested, curves of plasticizer concentration in white spirit versus immersion time are given as a function of irradiation time. Turning first to long term behavior, the migration phenomena are considered to reach an equilibrium or quasi-equilibrium state nearly after 60 days for specimens kept at 37°C (Fig. 2A), and 50 days for specimens kept at 50°C (Fig. 3A) or 70°C (Fig. 4A). On the other hand, it is easy to observe that in all cases irradiation pretreatment reduces slightly the plasticizer migration. Furthermore, continuation of the irradiation time from 5 to 10 days does not seem to result in any practical gains. This becomes also evident in Table I in which are quoted the equilibrium (or quasi-equilibrium) values of plasticizer migrated,
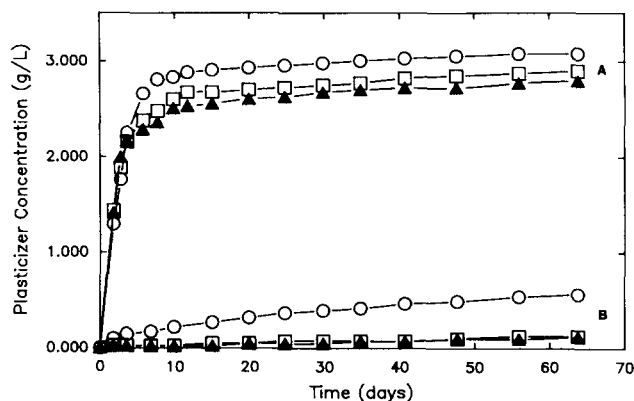
Figure 2 Plots of plasticizer concentration in white spirit and white oil vs. immersion time at 37°C as a function of irradiation time: (A) white spirit; (B) white oil; (O) untreated; (□) 5 days; (▲) 10 days.

Figure 4 Plots of plasticizer concentration in white spirit and white oil vs. immersion time at 70°C as a function of irradiation time: (A) white spirit; (B) white oil; (O) untreated; (□) 5 days; (▲) 10 days.

expressed as weight percentage of the initial amount contained.

It is worthwhile to mention that the migration behavior encountered for treated specimens (either for 5 or 10 days) against temperature follows an odd behavior, but in agreement with previous studies on migration for untreated material[14,15]: Longterm data suggest decrease of migration at 50°C and increase again at 70°C, showing a type of minimum (Fig. 2A, 3A, 4A, Table I). To explain this fact a mechanism consisting in an "annealing" effect has been already proposed and discussed in detail[15]: Together with plasticizer loss, which leads the system to a non-rubbery or nearly nonrubbery behavior, it is possible that an alteration of the polymer structure occurs during the immersion stage. Commercial PVC comprises a semicrystalline polymer and one cannot ig-
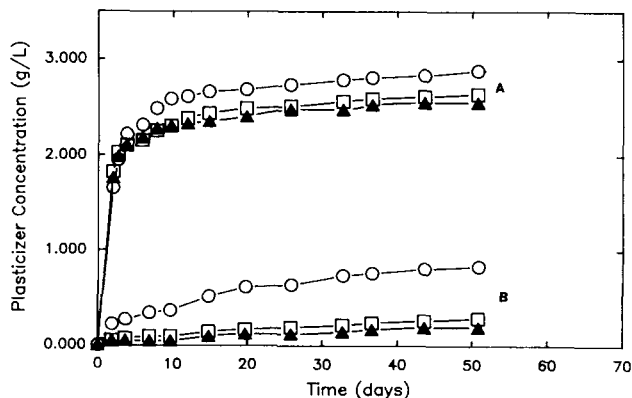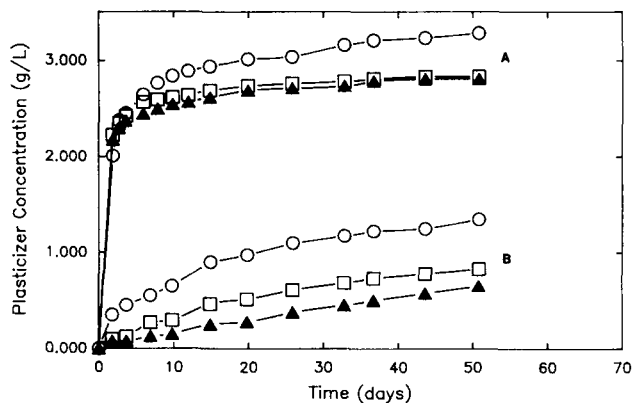
nore the effect of the very extended maintenance of the immersed material at the temperature levels considered. In other words, a rearrangement of the structure to a more ordered and compact scheme cannot be excluded while additional aging has to be expected, especially at higher immersion temperatures.

U.v. irradiation appears rather ineffective when considering short time data: At the early stages during which most of the plasticizer contained migrates, no improvement is observed, even for 10 days u.v. treatment.

Turning to kinetics aspects it was first attempted to test the data against typical Fickian models under the assumptions already made. Both eqs. (4) and (5) were used to find out good conformity, but only for the short times approximation (eq. 5) ($r^2 = 0.96$ to 1.00). On the other hand, the long times approximation provides correlation coefficients between 0.7 and 0.8.

In conformity with the aforementioned results, tests of M_t/M_∞ against t excluded any segmental relaxation control (Case II)[42,43]: Deviation from a linear relationship was obtained ($r^2 < 0.8$) and this was the result for all the media examined in this study, independently of temperature and irradiation time.

Kerosene

Similar observations can be made for specimens immersed in kerosene (Figures 5A, 6A, 7A, Table I) as irradiation time and immersion temperature influences migration behavior in the same trend as above described. Only long-term values are a little lower than the corresponding ones for white spirit

Figure 3 Plots of plasticizer concentration in white spirit and white oil vs. immersion time at 50°C as a function of irradiation time: (A) white spirit; (B) white oil; (O) untreated; (□) 5 days; (▲) 10 days.

Table I Equilibrium (or Quasi-Equilibrium) Values of Plasticizer Migrated as a Function of Immersion Temperature and Irradiation Time[a]

Immersion Temperature (°C)	37			50			70		
UV Irradiation Time (days)	0	5	10	0	5	10	0	5	10
Liquid environment									
White spirit	70.4	66.3	64.3	64.4	61.7	60.3	74.6	68.3	67.9
Kerosene	69.4	66.0	63.3	63.6	61.4	59.3	70.5	64.0	63.8
White oil	14.6	2.8	2.9	20.4	7.4	5.1	32.8	19.9	15.7
Lubricating oil	11.5	2.9	1.4	19.2	5.6	3.5	28.5	15.6	8.8

[a] All quoted values are expressed as weight percentage of the initial amount of plasticizer contained.

while the possible "annealing" effect was again observed. On the other hand, when considering the Fickian models the same results were obtained: Long-term approximation did not fit well ($r^2 < 0.85$) while the short times approximation provides the best fitting ($r^2 = 0.96$ to 1.00).

High Viscosity Media

White Oil

In Figures 2B, 3B, and 4B migration data are presented for white oil, a liquid environment of much higher viscosity. Independently of immersion temperature, migration is obviously restricted to much lower values. Equilibrium is considered to be reached nearly after 50 days for specimens immersed at 37 or 50°C (Fig. 2B, 3B), but maybe this is not true at the highest temperature (Fig. 4B) for the untreated samples. Nevertheless, in the latter case quasi-equilibrium conditions are supposed.

In contrast with the aforementioned low viscosity media, u.v. irradiation now appears to inhibit migration considerably. This becomes also evident in Table I. Furthermore, irradiation treatment for 5 days is adequate at 37°C and 50°C, but the picture seems to change when temperature increases to 70°C: Longer irradiation time results in some improvement.

In order to explain the latter behavior one has to reconsider the two different actions occurring when irradiating the PVC films: Degradation and cross-linking. Within our experimental conditions cross-linking seems to comprise the predominant aspect and for low immersion temperatures the surface layer of crosslinked material[13] remains effective in reducing migration. However, when the temperature increases the viscosity of the liquid environment decreases significantly and crosslinking requirements, in terms of network density, increase. Therefore,

the irradiation time for the highest immersion temperature, becomes an important aspect and this is the possible reason that here some differences between 5 and 10 days irradiation intervals appear.

Turning to the kinetics analysis it is worthwhile to mention that since most of the plasticizer remains in the material, the data obey Fickian kinetics. In other words, no transition to the glassy state, due to plasticizer removal, is expected.[12] Accordingly, both untreated and treated specimens appear to provide data fitting very well with short times approximation ($r^2 = 0.98$ to 1.00). On the other hand, satisfactory conformity to the longterm approximation ($r^2 = 0.96$ to 0.99) is also encountered in agreement with similar data presented by Kampouris in Ref. 2 and tested against kinetics models in Ref. 12.

Lubricating Oil

As seen from Figures 5B, 6B, 7B and also Table I specimens immersed in lubricant oil present the
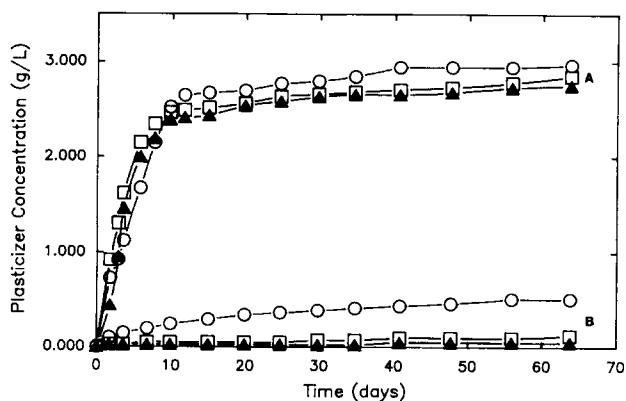

Figure 5 Plots of plasticizer concentration in kerosene and lubricating oil vs. immersion time at 37°C as a function of irradiation time: (A) kerosene; (B) lubricating oil; (O) untreated; (□) 5 days; (▲) 10 days.

lowest migration figures, but the total behavior follows that monitored for specimens tested in white oil: The reduction is satisfactory at the lower temperatures (Fig. 5B, 6B) in which 5 days u.v. treatment is sufficient. Nevertheless, at 70°C migration increases and extension of the irradiation time to 10 days seems to result in further improvement. On the other hand, the kinetics analysis results are exactly similar to those in white oil environment.

CONCLUSIONS

1. Within our experimental conditions, u.v. irradiation results in reducing or nearly preventing plasticizer migration when high viscosity oils are employed, especially at low temperatures. For low viscosity media the migration reduction was not important in agreement with a similar study in which migration in alcohols was examined after u.v. treatment up to 13 days.[13] The phenomenon was then associated with the partial failure of the protective top layer, which has been mainly attributed to alcohol counterdiffusion (i.e., liquid penetration into the plastic film).

2. The migration data collected, independently of temperature, fit satisfactorily the short-term Fickian approximation revealing the same behavior with that encountered in alcoholic media.[12,13]

3. In conjunction with the point (1) counterdiffusion processes have not been investigated up to now in this study. In agreement with results on counterdiffusion of the petroleum oils in untreated specimens[15] there is a pen-
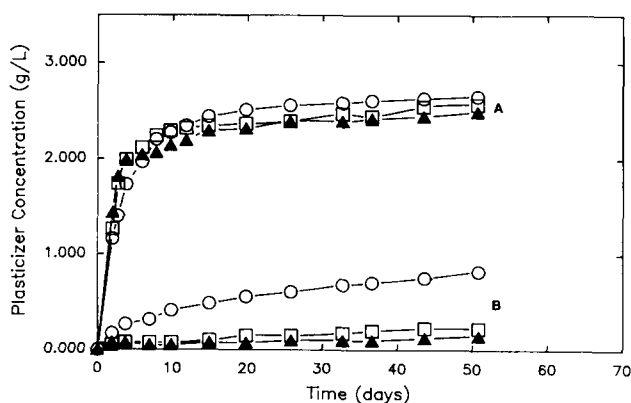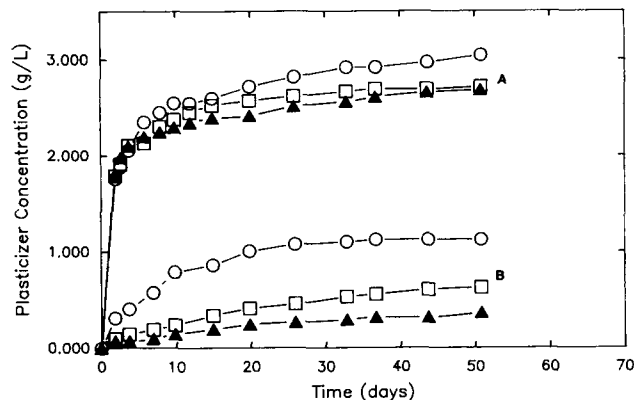

Figure 7   Plots of plasticizer concentration in kerosene and lubricating oil vs. immersion time at 70°C as a function of irradiation time: (A) kerosene; (B) lubricating oil; (○) untreated; (□) 5 days; (▲) 10 days.

etration activity, but reduced, also for the treated material. However, the phenomenon of the detached cross-linked layer remains a characteristic feature of the alcoholic media. In a following paper,[47] while presenting results on liquid penetration, we proceed in further discussion of the competitive aspects affecting the total behavior (i.e., diffusion (and counterdiffusion), "annealing," cross-linking and degradation), the latter considered during both u.v. irradiation and immersion stages.

REFERENCES

1. G. Haesen and A. Schwarze, Migration Phenomena in Food Packaging (a Literature Survey), Comm. Eur. Communities, (Rep.) EUR 5977 EN, 1978.
2. E. M. Kampouris, Eur. Polym. J., **11**, 705 (1975).
3. E. M. Kampouris, Rev. Gen. Caoutch. Plast., **52**, 289 (1975).
4. E. M. Kampouris, Polym. Eng. Sci., **16**, 59 (1976).
5. E. M. Kampouris, Paper No. 91, 4th European Conference on Plastics and Rubbers, Paris, June 1974.
6. J. R. Startin, M. Sharman, M. D. Rose, I. Parker, A. J. Mercer, L. Castle, and J. Gilbert, Fd Addit. Contam., **4**(4), 385 (1987).
7. D. Messadi and J. M. Vergnaud, J. Appl. Polym. Sci., **26**, 2315 (1981).
8. P. K. Dutta and K. R. Graf, J. Appl. Polym. Sci., **29**(6), 2247 (1984).
9. R. Schmolke, P. Kamenz, and H. G. Kramer, Acta Polym., **35**(1), 110 (1984).
10. K. Figge, Prog. Polym. Sci., **6**, 187 (1980).
11. G. S. Park and Tran Van Hoang, Eur. Polym. J., **15**(9), 817 (1979).

Figure 6   Plots of plasticizer concentration in kerosene and lubricating oil versus immersion time at 50°C as a function of irradiation time: (A) kerosene; (B) lubricating oil; (○) untreated; (□) 5 days; (▲) 10 days.

12. C. D. Papaspyrides, *J. Appl. Polym. Sci.*, **32**, 6025 (1986).
13. C. D. Papaspyrides, *Polymer*, **27**, 1967 (1986).
14. C. D. Papaspyrides and T. Duvis, *J. Appl. Polym. Sci.*, **38**, 1573 (1989).
15. C. D. Papaspyrides, *J. Appl. Polym. Sci.*, **38**, 1859 (1989).
16. K. H. Boo and T. M. Shaw, *J. Vinyl Technol.*, **9**(4), 168 (1987).
17. J. R. Startin, M. Sharman, M. D. Rose, I. Parker, A. J. Mercer, L. Castle, and J. Gilbert, *Food Addit. Contam.*, **4**(4), 385 (1987).
18. D. E. Till, R. C. Reid, P. S. Schwartz, K. R. Sidman, J. R. Valentine, and R. H. Whelan, *Food Chem. Toxic.*, **20**, 95 (1982).
19. H. W. Kretschmar, H. Paul, and P. Wuerthle (Kretschmar, Bruno, K.-G.) Ger. (East) Pat. 90428 (1972); *Chem. Abstr.*, **77**, 153406b.
20. P. J. Lyon and C. J. Clark (Marley Tile A.-G.) S. Afr. Pat. 71 06 168 (1973); *Chem. Abstr.*, **80**, 4503r.
21. G. E. Williams (Armstrong Cork Co.) U. S. Pat. 4 045 600 (1977); *Chem. Abstr.*, **87**, 153579s.
22. W. C. Vesperman, *J. Vinyl Technol.*, **1**(1), 1 (1979).
23. L. Ljunggren, *Artif. Organs*, **8**(1), 99 (1984).
24. M. Hirooka, Y. Fujii, T. Maruyama, and K. Hata (Sumitomo Chemical Co. Ltd.), Jpn. Kokai 75 129 701 (1975); *Chem. Abstr.*, **84**, 75281k.
25. M. Hirooka, Y. Fujii, K. Mashita, and F. Kimura (Sumitomo Chemical Co. Ltd.), Jpn. Kokai 75 148 503 (1975); *Chem. Abstr.*, **84**, 181298f.
26. Saken Kako Co. Ltd., Jpn. Kokai Tokkyo Koho JP 81 129 233 (1981); *Chem. Abstr.*, **96**, 36298z.
27. W. I. Congdon, J. J. Mottine and W. C. Vesperman (Western Electric Co. Inc.; Bell Telephone Laboratories Inc.) U. S. Pat. 4,166,881 (1979); *Chem. Abstr.*, **91**, 176418k.
28. P. Horn, F. Leppmeier, G. Eckert, and K. Fischer (BASF A.-G.) Ger. Offen. 2 630 114 (1978); *Chem. Abstr.*, **88**, 137616s.
29. P. Horn, F. Leppmeier, G. Eckert, K. Fischer, and H. Reimann (BASF A.-G.) Ger. Offen. 2 800 149 (1979); *Chem. Abstr.*, **91**, 158724c.
30. M. A. Oth and A. Mathieu, *Rev. Belge Matieres Plast.*, **9**(5), 307 (1968).
31. L. P. Nethsinghe and M. Gilbert, *Polymer*, **29**, 1935 (1988).
32. K. Tadashi, *Sci. Ind.*, **39**, 753 (1965).
33. M. Asai, K. Tsuda, and A. Okata (Agency of Industrial Sciences and Technology) Ger. Offen. 2 847 304 (1979); *Chem. Abstr.*, **91**, 21779e.
34. M. Asai, K. Tsuda, and H. Oka (Agency of Industrial Sciences and Technology) Jpn. Kokai Tokkyo Koho 79 64 573 (1979); *Chem. Abstr.*, **91**, 158573c.
35. M. Asai, Y. Suda, K. Imada, S. Ueno, and H. Nomura (Agency of Industrial Sciences and Technology; Shin-Etsu Chemical Industries Co. Ltd) Ger. Offen. 3 016 048 (1980); *Chem. Abstr.*, **94**, 31510m.
36. Toray Industries Inc., Jpn. Kokai Tokkyo Koho 80 121 049 (1980); *Chem. Abstr.*, **94**, 31627e.
37. Toray Industries Inc., Jpn. Kokai Tokkyo Koho 80 121 050 (1980); *Chem. Abstr.*, **94**, 31628f.
38. K. Imada, S. Ueno, Y. Nishina, and H. Nomura (Shin-Etsu Chemical Industry Co. Ltd), Fr. Demande 2 469 426 (1981); *Chem. Abstr.*, **95**, 170503v.
39. Mitsubishi Monsanto Chemical Co. and Shin-Etsu Chemical Industry Co. Ltd., Jpn. Kokai Tokkyo Koho JP 58 224 746 (83 224 746) (1983); *Chem. Abstr.*, **100**, 157910c.
40. Mitsubishi Monsanto Chemical Co. and Shin-Etsu Chemical Industry Co. Ltd., Jpn. Kokai Tokkyo Koho JP 58 224 800 (83 224 800) (1983); *Chem. Abstr.*, **100**, 157673c.
41. K.-P. S. Kwei, *J. Polym. Sci. A-1*, **7**, 1075 (1969).
42. J. Crank, *The Mathematics of Diffusion*, 2nd ed., Clarendon, Oxford, 1986, Chaps. 4 and 11.
43. T. Alfrey, E. F. Gurnee, and W. G. Lloyd, *J. Polym. Sci.*, **12**, 249 (1966).
44. A. D. Schwope, W. J. Lyman, and R. C. Reid, *Methodology for Estimating the Migration of Additives and Impurities from Polymeric Materials*, MIT Press, Cambridge, MA, 1984, Chaps. 2 and 3.
45. P. D. Calvert and N. C. Billingham, *J. Appl. Polym. Sci.*, **24**, 357 (1979).
46. D. Messadi and J. M. Vergnaud, *J. Appl. Polym. Sci.*, **27**, 3945 (1982).
47. C. D. Papaspyrides and T. Duvis, *Polymer*, **31**, 1085 (1990).
48. R. C. Reid, K. R. Sidman, A. D. Schwope, and D. E. Till, *Ind. Eng. Chem. Prod. Res. Dev.*, **19**, 580 (1980).
49. H. Sobue, Y. Tabata, and Y. Tajima, *J. Polym. Sci.*, **XXVII**(115), 596 (1958).
50. B. Ranby and J. F. Rabek in *Photodegradation, Photooxidation and Photostabilization of Polymers*, Wiley-Interscience, New York, 1975.