



An infrared spectroscopic study of the migration of a plasticiser in poly(vinyl chloride) resins

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Migration of a plasticiser, di-2-ethylhexylphthalate (DOP), in vinyl chloride resins containing stabilisers, di-*n*-butyl-tin-dilaurate and di-*n*-butyl-tin-maleate (DBTM) under heat, accelerated weathering (SWM), outdoor exposure or warm water immersion was investigated mainly by depth analysis using Fourier-transform infrared spectroscopy. In the case of heating, the DBTM inhibited the evaporation of DOP from the surface. Electron probe micro-analysis and scanning electron microscopy indicated that the concentration of the deteriorated DBTM near the surface formed a barrier layer against the evaporation of DOP. Under the other conditions, migration of the DOP was different from that of heating, and the DBTM did not affect the evaporation of DOP. Under SWM, the evaporation of DOP was observed only from the exposed side, while it was observed from both sides under outdoor exposure. Moreover, the depth profiles of DOP in the samples exposed outdoors were similar to that of the immersed samples, which suggested that the plasticiser was extracted by water such as rainfall and dew, during the outdoor exposure.

INTRODUCTION

Poly(vinylchloride) (PVC), which is used widely as a commercial plastic, generally contains plasticisers and stabilisers in order to provide plasticity and stability to the polymer. It is well known that plasticisers migrate in the resin under heating conditions, and that a part of the plasticiser is lost from the resin.^{1–4} It is to be expected that the distribution of plasticiser in the degraded PVC thus differs from that in normal PVC. Because a change in the condition of the plasticiser directly influences the properties of PVC articles, there have been many studies on the migration or loss behaviour of the plasticisers from PVC. However, most of these have been based on weight loss,^{1,2} or decrease in the quantity of plasticiser.^{3,4} Also, there have been no published studies on the changes in the distribution of plasticiser in PVC since no

suitable methods are available for this type of evaluation.

For depth analysis of metals or inorganic materials, dynamic secondary ion mass spectroscopy (SIMS) and auger electron spectroscopy (AES) have been widely used. However, these techniques are not appropriate for the analysis of organic materials such as PVC. Recently, we have developed a method of depth analysis which combines the cutting technique with a microtome and the micro-analysis technique by Fourier-transform infrared spectroscopy (FT-IR).⁵ This method enables the measurement of the distribution of the functional groups in the depth direction with micrometer resolution, and has been applied to studies of the degradation of various materials.⁶ This paper describes the investigation of the migration of plasticiser in PVC and stabiliser effects under conditions of heating, accelerated weathering, outdoor exposure, and immersion in warm water, using the developed depth analysis method.

EXPERIMENTAL

Materials

Di-2-ethylhexylphthalate (DOP) was used as plasticiser. Di-*n*-butyl-tin-dilaurate (DBTDL) and di-*n*-butyl-tin-maleate polymer (DBTM) were used as stabilisers. By addition of these additives to PVC ($M_w = 130\,000$), two kinds of compounds with different stabilisers were prepared using a Henschel Mixer at 110°C. Subsequently, the compounds of plasticised PVC were injected into a dumb-bell shape 3 mm in thickness. The composition of the samples is shown in Table 1.

Samples were subjected to various conditions, heating in air, accelerated weathering (SWM), outdoor exposure, and warm water (60°C) immersion.

Table 1. Composition of the plasticised PVC

Sample	Plasticiser (phr)	Stabiliser (phr)
A	DOP (40)	DBTDL (2)
B	DOP (40)	DBTM (2)/DBTDL (1)

Analysis

The depth distribution of DOP in PVC was measured by depth analysis using FT-IR, and those of the stabilisers by electron probe microanalysis (EPMA).

Principle of depth analysis

This method combines the cutting technique using a microtome with the micro-analysis technique using FT-IR. The principle of the method is shown in Fig. 1.

- (1) Microtome cutting: samples are cut obliquely into thin films having a thickness of 1–2 μm to increase the apparent depth. When the cutting angle (θ) is 1°, the length of the cutting surface (l) is 50 times the corresponding depth (d).
- (2) Line analysis by FT-IR: the thin films are analysed in the depth direction by IR microspectroscopy in the transmittance mode or a micro-ATR technique.⁷ The micro-ATR prism has a unique shape as shown in Fig. 2. By setting this prism on the transmitting IR pathway of an IR microscope, material surfaces can be

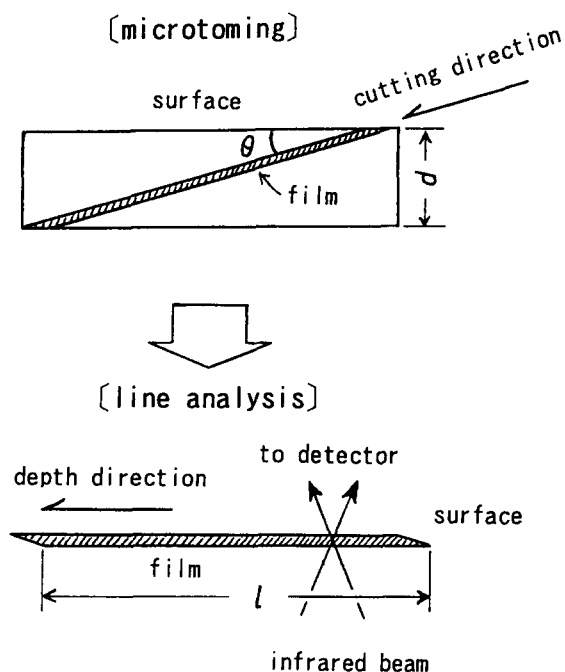


Fig. 1. Principle of depth analysis.

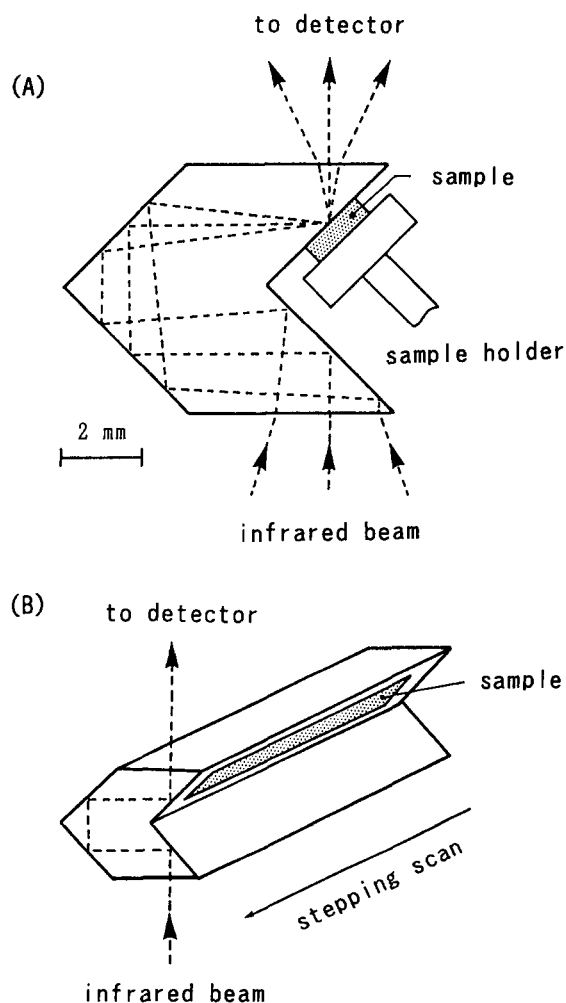


Fig. 2. Schematic drawing of the prism developed for ATR IR microspectroscopy. (A) Cross-section of ATR prism (zinc selenide), and (B) line analysis method.

analysed in the order of a 10-micrometer spatial resolution. Therefore, by applying the cutting surfaces in direct contact with the prism, the samples can be analysed in the depth direction as in the transmittance mode. This technique is very useful for the analysis of soft samples such as plasticised PVC.

- (3) Depth resolution: when θ is 1° and the line analysis is performed at $100\ \mu\text{m}/\text{step}$, the depth resolution is expected to be $2\ \mu\text{m}$. Actually, when measuring a two-layer-coating, $2\ \mu\text{m}$ has been the highest depth resolution attainable.

Apparatus

For cutting, a MICROM HM-350 microtome or a YAMATO CR-500 microtome was used; for line analysis, a JOEL JIR-100 FT-IR equipped with a MAU-110 IR microscope, an AMS-110 auto-mapping stage and a mercury-cadmium-tellurium (MCT) detector was used; for measuring the distribution of stabilisers, a SHIMADZU EPM-810 EPMA was used; and for observing the morphology of surfaces and sections, an AKASHI ISI-DS130 scanning electron microscope (SEM) equipped with energy dispersion spectroscopy (EDS) was used.

RESULTS AND DISCUSSION

Plasticiser migration by heating

Weight loss

The weight loss of the samples due to heating is plotted in Fig. 3. The weight loss of sample A, which contains DBTDL as a stabiliser, is not linear against heating time but Fig. 4 shows that

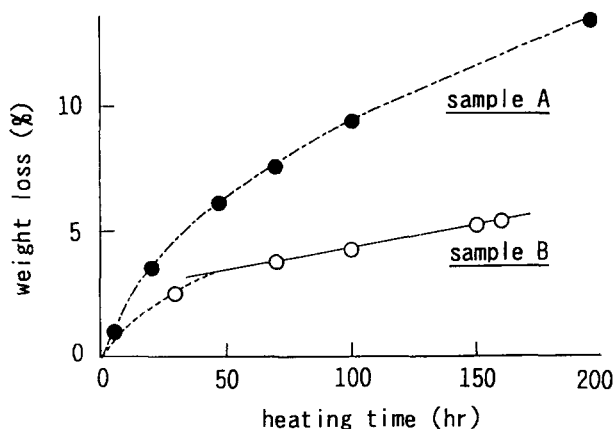


Fig. 3. Weight loss of plasticised PVC on heating at 120°C .

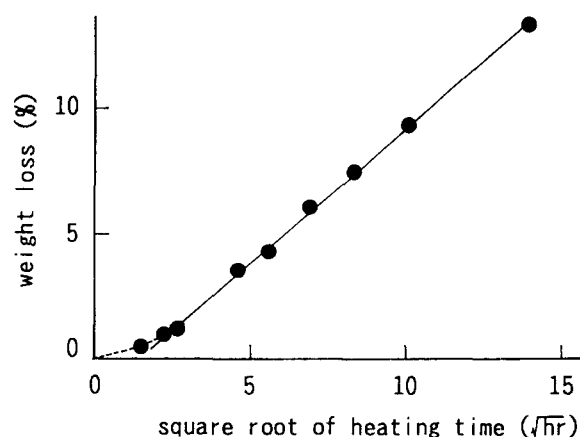


Fig. 4. Weight loss of sample A on heating at 120°C versus square root of heating time.

the weight loss is linear with the square root of the heating time after *c.* 7 h. On the other hand, sample B, which contains DBTDL and DBTM as stabilisers, loses weight at a lower rate than sample A, showing a linear weight loss against heating time after *c.* 50 h. It is generally known that the weight loss of a polymer is linear with the square root of time when the rate of plasticiser loss is controlled by a diffusion process, and linear with time when the rate is controlled by an evaporation process.^{1,2} These data therefore suggest that the DOP loss mechanisms in the two samples are different.

Depth distribution of DOP

To clarify the phenomenon of weight loss, the depth distribution of DOP was measured. Depth profiles of DOP in samples A and B, heated at 120°C , are shown in Figs 5 and 6, respectively. In

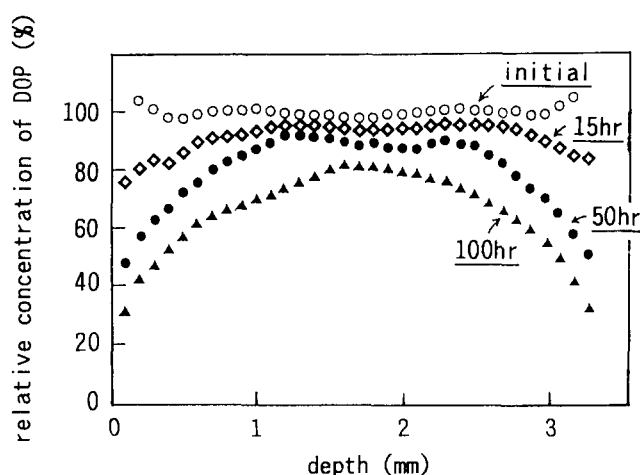


Fig. 5. Depth profiles of DOP in PVC (sample A) heated at 120°C .

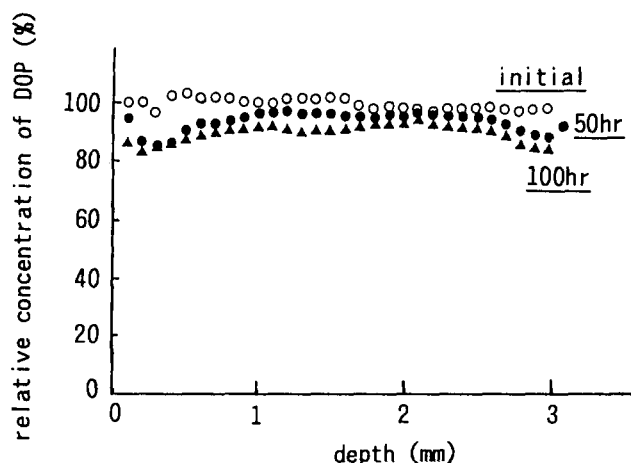


Fig. 6. Depth profiles of DOP in PVC (sample B) heated at 120°C.

sample A, DOP seems to be lost first from the surface, and then seems to diffuse from the interior of the polymer to the surface. This is a typical pattern of diffusion control. On the other hand, DOP loss from sample B is smaller, and the slope of the distribution is small. This pattern indicates that the rate of evaporation from the surface is smaller than that of diffusion in the polymer. This is the pattern for surface control. In short, these distribution data actually prove the usual explanation for weight loss data.

Action of stabilisers

To clarify the reason for the different loss mechanisms of DOP between samples A and B, due to the different stabilisers, the actions of the stabilisers were investigated by EPMA, SEM, and FT-IR.

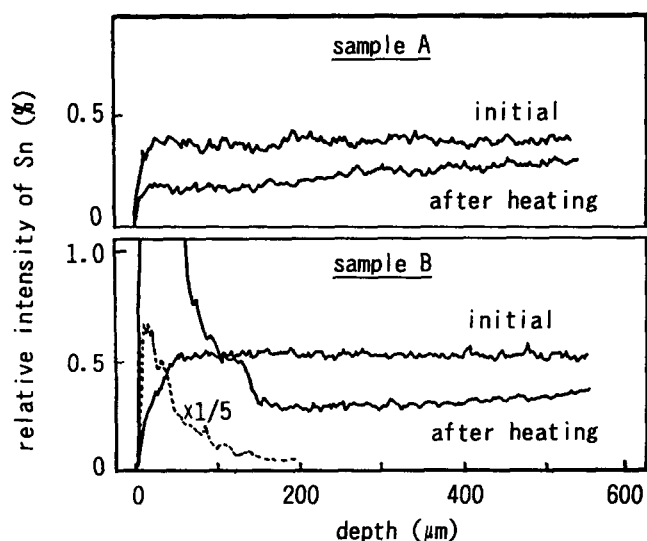


Fig. 7. Sn distributions in PVC heated at 120°C.

The distributions of tin in samples A and B, measured by EPMA, are shown in Fig. 7. On heating sample A, Sn decreases in the region close to the surface. However, the Sn in sample B is remarkably concentrated near the surface. Figure 8 shows the SEM images of the surfaces and sections. It was found that phase separation occurred near the surface in sample B on heating, and that a deposit formed on the surface (see Fig. 8(b) and (b')). In sample A, on the other hand, no change occurred on heating (see Fig. 8(a) and (a')). The separated phase exists from the surface to a depth of about 100 μm , and this depth is similar to the EPMA result. Furthermore, a large quantity of Sn was detected in the deposit and the separated phase.

For further clarification of their components, the deposit and the separated phase were analysed by FT-IR. An ATR spectrum of sample B heated at 120°C for 100 h is shown in Fig. 9. This spectrum indicates that the deposit on the surface is not the stabiliser itself but deteriorated stabiliser. A depth profile of this material, obtained using an IR microscope, is shown in Fig. 10. The material is distributed to a depth of about 50 μm , which is similar to the Sn distribution obtained by EPMA. The results suggest migration of DBTM in the polymer and its concentration near the surface in the deteriorated form. Thus, it seems that the concentrated material formed a barrier layer against the evaporation of DOP from the surface.

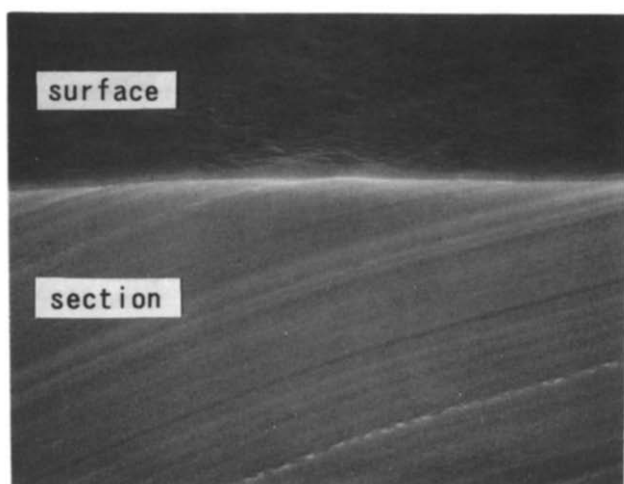
Thus, under the heating conditions, the migration of DOP was affected by the stabiliser. Successively, the migration of DOP under the other conditions and the effects of stabilisers were investigated.

Migration of plasticiser during SWM or outdoor exposures

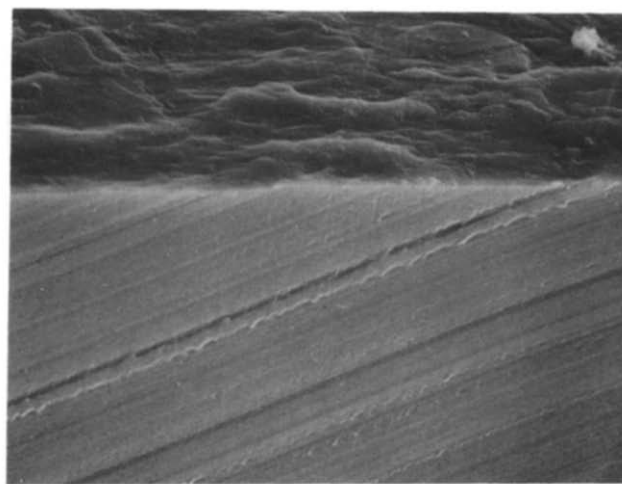
Weight loss and plasticiser distribution

The curves of weight loss of sample B during SWM and outdoor exposures are shown in Fig. 11. For SWM, the weight loss is linear with testing time which is similar to that due to heating. For outdoor exposure, it is also linear against exposure time, though there is a seasonal fluctuation.

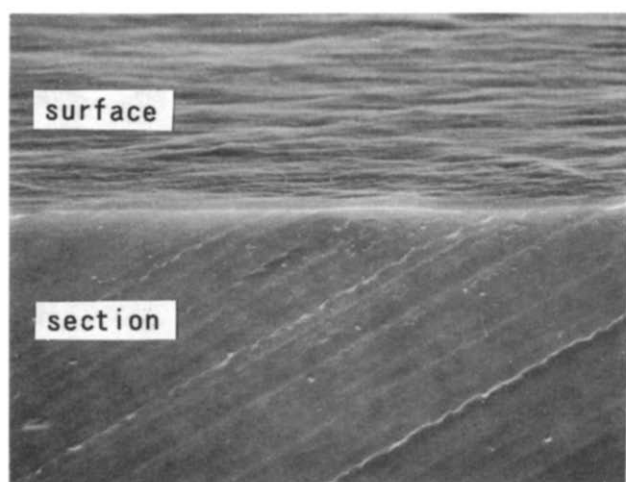
The depth profiles of DOP in sample B degraded by SWM, shown in Fig. 12, indicate that DOP is lost from the exposed surface, to a depth of about 800 μm . The depth profiles of



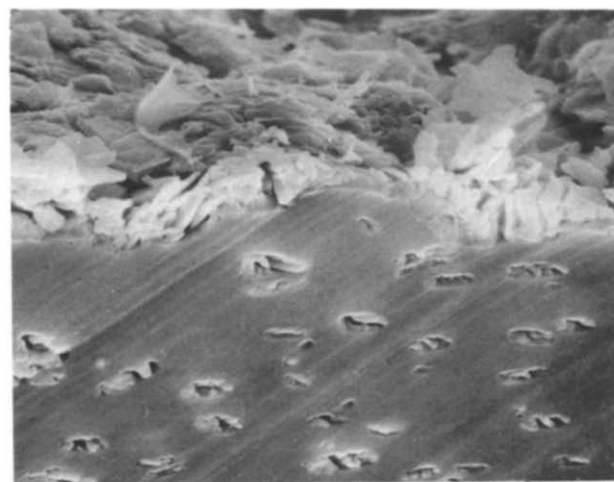
(a) sample A - initial



(a') sample A - after heating



(b) sample B - initial



(b') sample B - after heating

5 μm

Fig. 8. Changes of SEM images of the surfaces and sections by heating samples at 120°C.

DOP in the same sample degraded by outdoor exposure shown in Fig. 13 indicate that DOP is lost from both surfaces. This difference in the depth distributions of DOP suggests that there is a different migration mechanism for DOP between SWM and the outdoor exposures.

From the weight loss data only, the mechanism of DOP weight loss by SWM and outdoor exposure seems to be same as that for heating, that is, surface controlling. However, Figs 12 and

13 demonstrate that it is not a surface-controlled process. This result indicates that the loss mechanism for additives must be investigated by using not only weight loss but also their distribution.

Action of stabilisers

Under the heating conditions, DBTM strongly affects the evaporation of DOP from the surface of sample B, which results in a rather

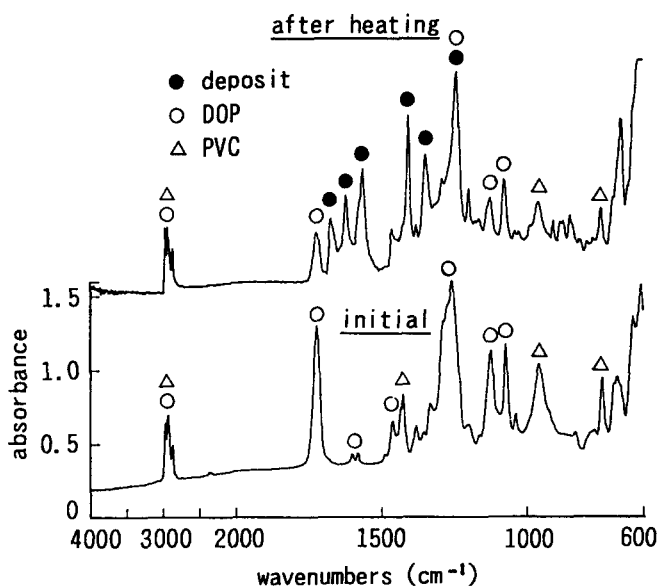


Fig. 9. ATR spectrum of sample B heated at 120°C for 100 h. Prism, KRS-5; upper line, after heating; lower line, initial.

homogeneous distribution. Under weathering conditions such as SWM and outdoor exposure, on the other hand, the stabiliser did not seem to affect the evaporation of DOP. The action of stabilisers under the weathering conditions was therefore investigated by EPMA. The distributions of Sn obtained by EPMA shown in Fig. 14 indicate that the large Sn concentration, observed under the heating conditions, does not appear though there is a slight concentration on the surface. The SEM images of the surface and section in Fig. 15 show no separated phase or deposit which was observed in the heated

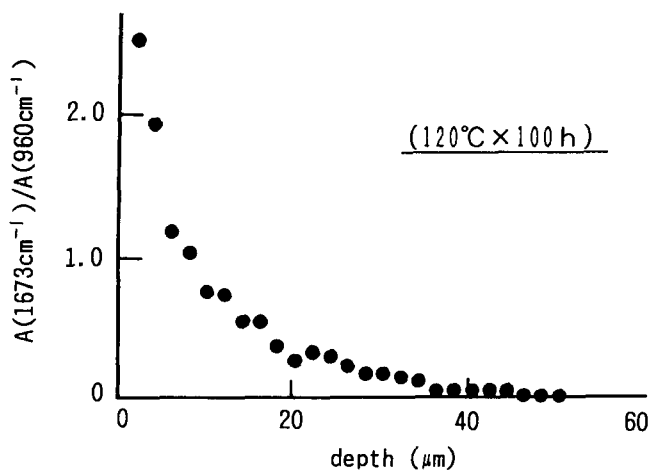


Fig. 10. Depth profile of the deposit obtained by IR microspectroscopy.

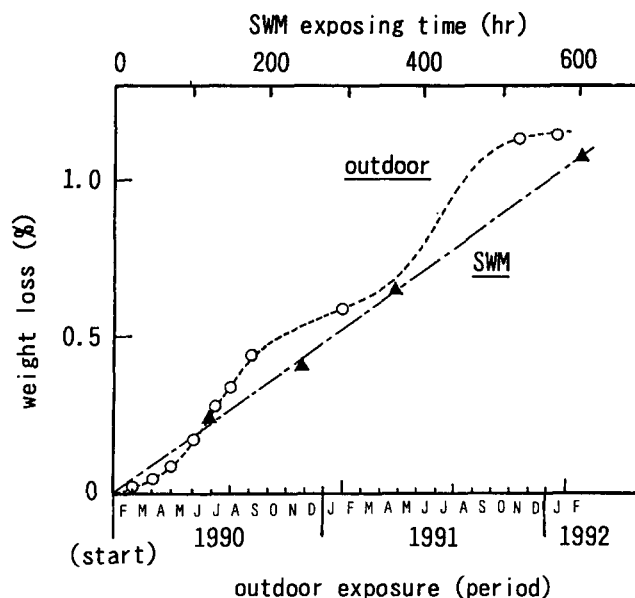


Fig. 11. Curves of weight loss of sample B due to SWM and outdoor exposure.

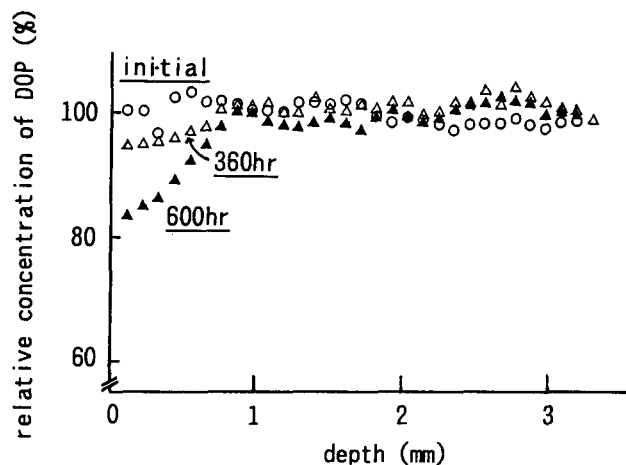


Fig. 12. Depth profiles of DOP in sample B exposed to SWM.

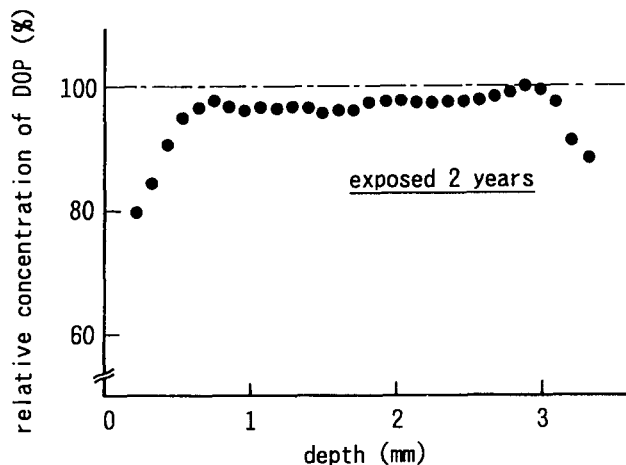


Fig. 13. Depth profile of DOP in sample B due to outdoor exposure.

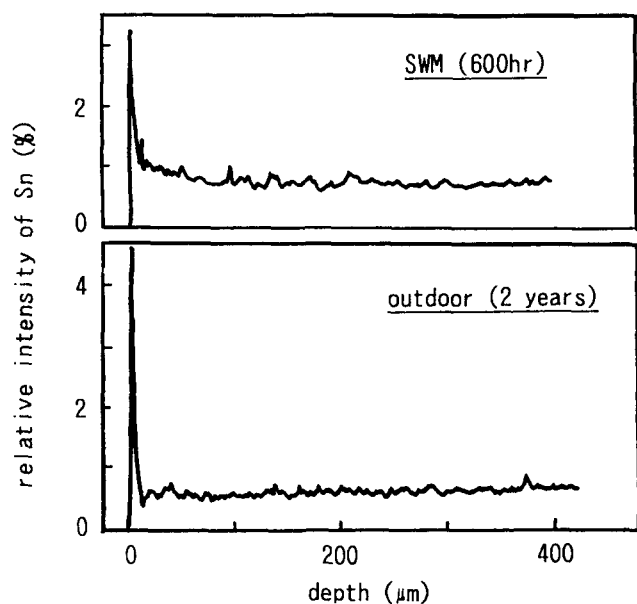


Fig. 14. Sn distributions in sample B exposed to SWM or outdoor.

sample. The results suggest that one of the reasons why DBTM does not affect the evaporation of DOP under weathering conditions is the slow migration of DBTM at ambient temperature.

Migration of plasticiser by immersion in water

The depth profile of DOP in PVC immersed in water is shown in Fig. 16. This figure demonstrates that DOP is lost from both surfaces as is the case of outdoor exposure. This result suggests that DOP in PVC exposed outdoors is lost mainly by water such as rainfall or dew. Therefore, the difference in the depth distribu-

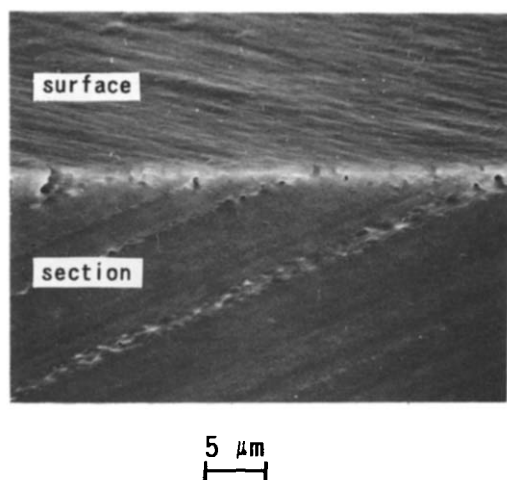


Fig. 15. SEM image of sample B exposed to SWM for 60 h.

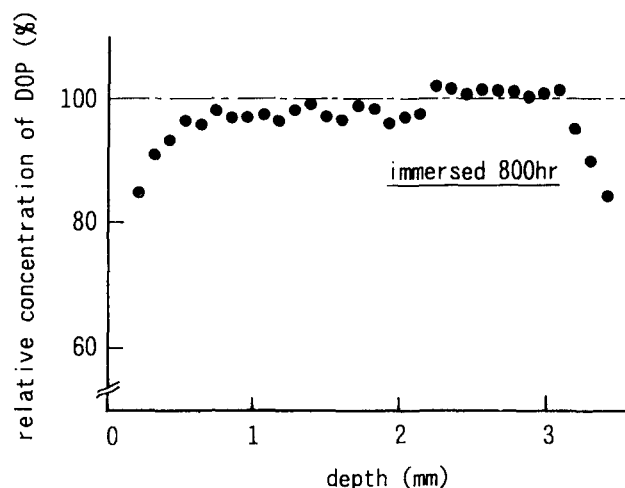


Fig. 16. Depth profile of DOP in sample B immersed in warm water at 60°C for 800 h.

tion between SWM and outdoor exposures described in the previous section is probably due to the difference in water spraying conditions.

CONCLUSIONS

By depth analysis of DOP in PVC containing stabilisers, DBTM and DBTDL, the migration of plasticiser in PVC was clarified as follows.

- (1) Under heating conditions, the DBTM stabiliser migrated in the polymer and concentrated near the surface with deterioration. The concentrated materials inhibited the evaporation of DOP from the surface.
- (2) Under other conditions of SWM, outdoor exposure, and immersion in warm water, the change in DOP distribution differed from that under heating conditions. In these cases, the stabiliser did not affect the behaviour of DOP.
- (3) The depth distribution of DOP in PVC immersed in water was very similar to that in PVC exposed outdoors. The results suggested that DOP in PVC exposed outdoors was mainly lost by extraction by water, such as rainfall and dew.
- (4) The depth distribution of DOP in SWM-tested PVC differed from that in PVC exposed outdoors. This was assumed to be the result of the difference in water spraying conditions.

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