Migration of Plasticizer in Vinyl Resins: An Infrared Spectroscopic Study

Additives in resins and plastics provide some desirable properties that are important in the end use of these materials. However, for additives to be effective, it is important that they remain in the plastic or resin for sufficient periods of time. This is especially true for plasticizers that are added to vinyl resins, the loss of which makes the resin inflexible. Effectively, plasticizers behave as low volatile solvents for the resin. The "permanence" of a plasticizer is determined by (a) its solvent properties *vis-à-vis* the resin and (b) loss due to volatilization, extraction, and by other means. This is physically manifested by movement of the plasticizer from the bulk of the resin to its surface and the loss from the surface into the surrounding medium. The mechanisms of these two processes are distinct and dependent on different properties of the plasticizer, e.g., the migration within the resin is dependent on the viscosity of the plasticizer and its loss from the surface to the atmosphere is dependent on vapor pressure.[1]

All of the work described in the literature on migration of plasticizers has involved the measurement of decrease in weight of the plasticized resin in contact with various interfaces such as vacuum, oils, solvents, soapy water, etc.[2,3] In this communication, we report a spectroscopic method that can monitor the migration of the plasticizer in the bulk of the vinyl resin. The advantage of such a method is that it is specific to the plasticizer, convenient, and can be extended to other additives.

The basic experimental strategy is to create a plasticizer-free region near the surface of a plasticized resin and then follow the migration of the plasticizer from the bulk into this region by attenuated total reflection-infrared spectroscopy (ATR-IR).[4] The penetration depth of the infrared evanescent wave into the resin is dependent on the wavelength but is of the order of a few microns and effectively defines our sampling depth. The experimental procedure involves contacting a 50-mil-thick plasticized PVC film with ethanol for 2 to 3 min. This dissolves away the plasticizer from the surface layers of the resin creating a concentration gradient of the plasticizer. The infrared spectrum of the surface layers are then recorded as a function of time using a KRS-5 crystal (50 × 5 × 2 mm, 45°) mounted on a Harrick ATR accessory in a Digilab FTS-20 FTIR Spectrometer. Typically, 200 scans at a resolution of 4 cm^{-1} were recorded for each time frame. The PVC resin studied contained 35 parts per hundred parts of resin of a phthalate plasticizer. The ethanol treatment removed only about 0.1 wt. % of the material from the resin. IR measurements on the extract confirmed that only the plasticizer was removed.
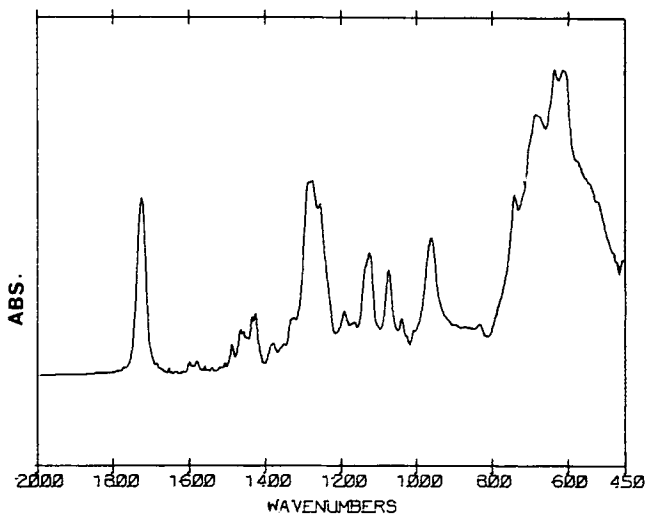

Fig. 1. ATR-IR spectrum of plasticized PVC film.

CCC 0021-8995/84/062247-04$04.00

TABLE I
List of Frequencies in Plasticized PVC and Their Assignments[a]

Frequency (cm^{-1})	Assignment[b]	Frequency (cm^{-1})	Assignment[b]
2800–3000	C—H stretch	1125	C—O stretch; PL
1725	C=O stretch; PL	1075	C—C stretch; PVC
1600 ⎫	C—C stretch	1040	C—C stretch, PL
1580 ⎬	aromatic	960	CH$_2$ rock, PVC
1490 ⎭	PL	740	CH out of plane, PL
1465	—CH$_2$—wag. PL	690	—
1437 ⎫	CH$_2$ wag. PVC	640 ⎫	C—Cl stretch; PVC
1425 ⎭		615 ⎭	
1380	CH$_3$ bend, PL		
1330	CH$_2$ twist, PVC		
1275–1290	C—O stretch; PL		
1255	H—C—Cl bend; PVC		
1190	PL		

[a] Functionalities with the greatest contribution to the potential energy distribution are shown.
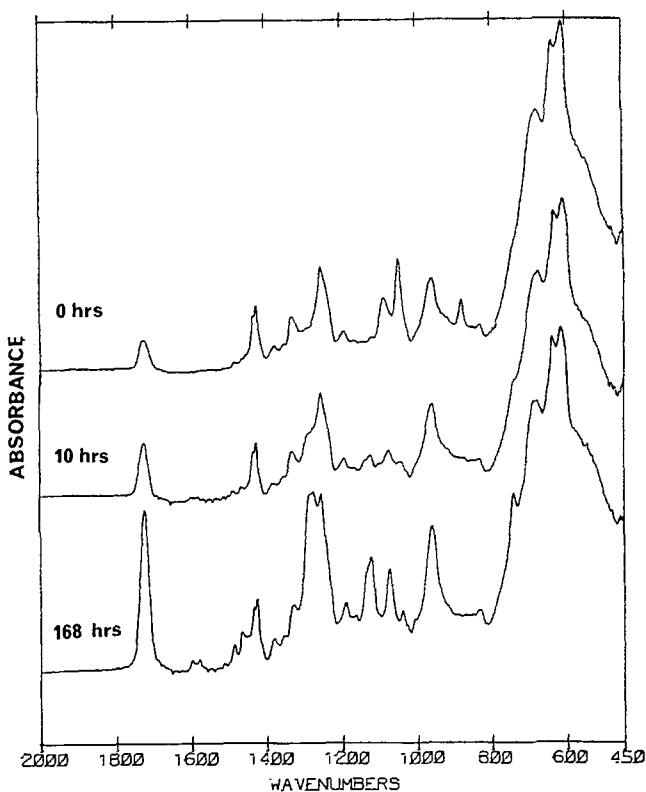[b] PL = plasticizer; PVC = poly(vinyl chloride).

Fig. 2. ATR-IR spectrum of PVC film immediately upon extraction, 10 h after extraction, and 168 h after extraction.
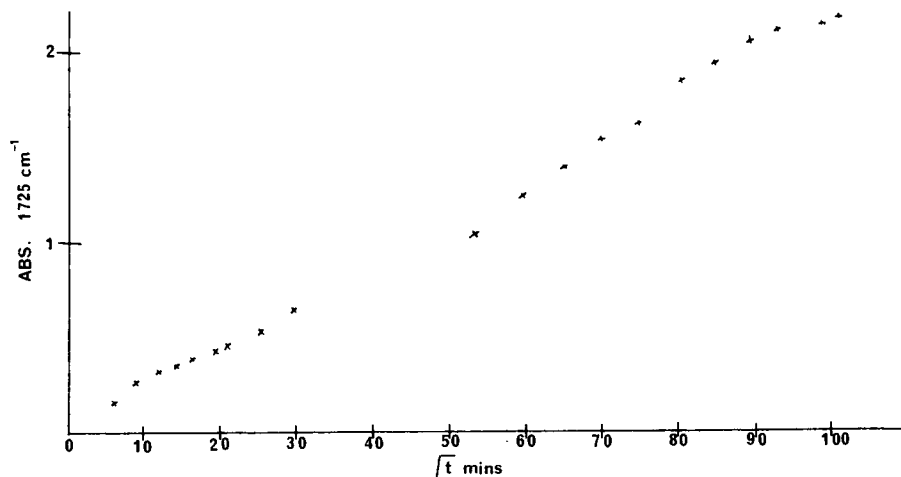
Fig. 3. Plot of the absorbance of 1725 cm^{-1} band of plasticizer as a function of time.

Figure 1 shows the ATR-IR spectrum of the plasticized,PVC resin and the vibrational band assignments are shown in Table I.[5] Figure 2 shows the ATR-IR spectra of the plasticized PVC film immediately after extraction, 10 h after extraction, and 168 h after extraction. It is clear from this figure that all of the vibrational bands due to the plasticizer are absent immediately upon extraction and gradually grow in as a function of time. (The residual band at 1725 cm^{-1} is due to the PVC resin.) Effectively, we are measuring the migration of the plasticizer into the plasticizer-free region in real time.

The simplest model predicts that the migration of the plasticizer within the bulk of the resin is diffusion-controlled, in which case the mass of plasticizer moving into the plasticizer free region is governed by

$$\text{mass} = C_0 K (D_A t)^{1/2} \tag{1}$$

where C_0 is the bulk plasticizer concentration, D_A the diffusion constant, K a constant, and t is time. Small has shown from studies on evaporative loss of plasticizers that eq. (1) holds true (i.e., D_A is a constant) for small losses of plasticizer (up to 20–30% range).[6] Since we are dealing with losses of plasticizer in the ~0.5% range, eq. (1) is expected to hold true.

Since the absorbance of the infrared absorption band is directly proportional to the concentration of the absorbing species, monitoring the growth in intensity of the plasticizer bands gives a direct estimate of the amount of plasticizer migrating into the plasticizer free region. Since the band at 1725 cm^{-1}, which is due to the C=O stretch of the ester group, is a prominent band in the infrared spectrum of the plasticizer, we monitored the increase in absorbance of this band as a function of time. The absorbance was corrected for the contribution from the PVC resin and ratioed against the 1425 cm^{-1} band of the PVC resin to take into account any alignment changes during subsequent runs.

Equation (1) predicts that the increase in absorbance of the plasticizer bands should be proportional to the square root of time. Figure 3 is a plot of the absorbance of the 1725 cm^{-1} band as a function of the square root of time. The plot indicates that, as a first approximation, the migration of this plasticizer is diffusion-controlled. The slope of this line is proportional to the diffusion constant of the plasticizer.

These experiments, therefore, suggest that ATR-IR is a convenient and direct method for following the migration of plasticizers in PVC resins. Such experiments can also be extended to study the migration of other additives and can also be modified to follow the migration of plasticizer from thin strips of resin (~1 mil) into materials such as food, etc., in contact with the resin.[7]

References

1. H. M. Quackenbas, *Ind. Eng. Chem.*, **46,** 1335 (1954).
2. E. M. Kampouris, *Polym. Eng. Sci.*, **16,** 59 (1976).
3. M. C. Reed, H. F. Klemm, and E. F. Schultz, *Ind. Eng. Chem.*, **46,** 1344 (1954).
4. N. J. Harrick, *Internal Reflection Spectroscopy*, Wiley, New York, 1967.
5. W. H. Moore and S. Krimm, *Spectrochim. Acta*, **29A,** 2025 (1973).
6. P. A. Small, *J. Soc. Chem. Eng.*, **66,** 17 (1947).
7. D. E. Tell, R. C. Reid, P. S. Schwartz, K. R. Sidman, J. R. Valentine and R. H. Whelan, *Food Chem. Toxicol.*, **20,** 95 (1982).

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