Graphical Abstract

Diffusion of di(2-ethylhexyl)phthalate in PVC quantified by ATR-IR spectroscopy

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Department of Chemical and Life Science Engineering, Virginia Commonwealth University, 601 West Main Street, Richmond, Virginia 23284

Abstract

Di(2-ethylhexyl) phthalate (DEHP) is a commonly employed plasticizer for poly(vinyl chloride) (PVC). Diffusion of di(2-ethylhexyl) phthalate (DEHP) takes place when plasticized PVC is immersed in hexane. Rather than determining DEHP concentration in the immersion solvent, an IR window for PVC from 1500 - 1900 cm^{-1} enabled direct measurement of HADD (hexane assisted DEHP diffusion) using ATR-IR by monitoring the DEHP carbonyl absorption at 1715 cm^{-1} . The present study employed PVC containing 45% plasticizer (PVC-45, tygon tubing). A fast diffusion process was observed for short times (< 30 s) while a slower diffusion process occurred at longer immersion times ($30 \text{ s} < t < 6 \text{ min}$). A synergistic increase in mesosurface T_g toward that of PVC coupled with low solubility of hexane in PVC accounts for decreased DEHP diffusion rates (10^{-12} - $10^{-13} \text{ cm}^2 \text{ sec}^{-1}$) for immersion times > 30 sec. Analysis by XPS shows the outermost surface is PVC free of plasticizer after 6 min immersion. After an induction period, back diffusion coefficients D_b were estimated from peak areas during a subsequent fast recovery period (10^{-14} - $10^{-15} \text{ cm}^2 \text{ sec}^{-1}$). A model is proposed for the induction period associated with re-plasticization that involves a change from a mesosurface glass to a gel like solid.

Introduction

Diffusion is a widely studied phenomenon with examples including small molecules traversing polymer solids in gas diffusion membranes[1] and large molecules diffusing from polymeric solids for drug delivery.[2] Diffusion may cause a change in state such as the diffusion of Ca^{2+} that leads to the formation of a liquid

crystalline gel.[3] A more subtle change occurs by the formation of an interphase during diffusion of two miscible polymers, namely low molecular weight liquid

polystyrene into a glassy poly(phenylene oxide).[4] In the present study, the short time hexane assisted diffusion of plasticizer (HADD) from a gel-like rubbery solid results in the formation of a glassy mesosurface (~1000 nm). This change of state for the mesosurface coupled with greatly diminished solubility of the solvent in the glass greatly slows the diffusion of plasticizer into the depleted surface zone.

The system studied herein is well-known plasticized polyvinyl chloride (PVC, **1**), which ranks among the leading commodity polymers.[5] PVC has a glass transition temperature of ~81°C[6, 7] and a melting transition ~165 - 217 °C depending on molecular weight.[8] A plasticizer is employed to lower T_g and increasing flexibility, workability and extensibility.[9] Di(2-ethylhexyl)phthalate (DEHP, **2**) has been the most often used plasticizer. Varying DEHP content results in increasing modification from tough/hard (~10 wt%) to soft/flexible (40 wt% or higher).

PVC has low crystallinity due to heterotacticity.[10, 11] ATR-IR analysis by Koenig[12] suggested that percent crystallinity is not affected by plasticization. That is, DEHP plasticization is associated with one or more amorphous PVC domains. In particular, Koenig noted the constant ratio of band intensities of two methylene deformations at 1435 and 1427 cm^{-1} and interpreted this observation as evidence for the same degree of crystallinity in PVC and PVC plasticized by DEHP. Diffraction studies of Geil revealed processing dependent morphologies with DEHP heterogeneously distributed after low temperature processing and more homogeneously distributed after processing at higher temperatures.[13] Unplasticized regions were little affected by processing conditions studied.

Tygon tubing is a well-known example of plasticized PVC. Since DEHP is not covalently bound, DEHP diffusion occurs in contact with lipophilic media.[14, 15] Migration of DEHP and other phthalate ester plasticizers has been a matter of concern.[16, 17] DEHP and other phthalate ester plasticizers have low acute toxicity but long term studies suggest chronic effects.[18] DEHP is a peroxisome proliferator (PPs) and is characterized as a non-genotoxic rodent carcinogen. Rats and mice develop adenomas and carcinomas after prolonged feeding with DEHP, but “limited DEHP-specific human data are available, even though exposure to DEHP and other phthalates is common in the general population. This likely constitutes the largest gap in our knowledge on the potential for DEHP to cause liver cancer in humans.”[19] These concerns have resulted in exploration of alternative plasticizers such as succinate diesters[20] and oligo isosorbide esters.[21] In a different and highly effective approach, covalently binding plasticizers completely eliminates migration.[22]

Plasticizer diffusion has been the subject of studies based on analysis of liquids to which PVC is exposed. After solvent exposure, rates of diffusion have been determined by analysis of

DEHP in the extraction solvent the using HPLC or UV-Visible spectroscopy. Recent studies include DEHP diffusion into media such as water[23] or aqueous organic solvents.[24]

Pentane was studied by Vergnaud as a solvent for extraction of DEHP.[25] Rates of diffusion were determined as a function of immersion time by HPLC. Diffusion coefficients were determined at 40, 50 and 60 °C by applying Fick's second law.[26] Taverdet and Vergnaud found that exposure of DEHP plasticized PVC to hydrocarbon solvents resulted in a metastable near-surface DEHP depletion zone.[27, 28] That is, after hexane assisted DEHP diffusion (HADD), a metastable glass-like surface layer presented a barrier to further diffusion from the bulk.[29] Methanol can also be used to develop this metastable near surface depleted zone.[30] Considering the concentration of DEHP can be 40-50 wt%, the presence of this barrier-glass is an important finding. More recently, PVC was surface-depleted of DEHP plasticizer followed by overcoating with poly(ethylene glycol). The PEG overcoat provided a barrier for DEHP diffusion.[25]

Rather than determining DEHP concentration in the immersion solvent, the present study examines near surface DEHP concentration directly by ATR-IR. An IR window for PVC at 1715 cm^{-1} was critical as this is the carbonyl absorption frequency for DEHP. The effective quenching of DEHP diffusion after emersion from hexane enables obtaining ATR-IR peak areas at ambient temperature as a function of immersion time with negligible change in absorbance for at least 12 hours. Diffusion coefficients, D , were determined from DEHP carbonyl peak areas after immersion in hexane. Interestingly, distinct diffusion processes were found after short (< 20 s) and longer time ($20\text{ s} < t < 6\text{ min}$) hexane immersion.

Subsequent back diffusion of DEHP from the bulk "reservoir" into the depleted near surface is temperature dependent. After short hexane immersion times (< 20 s), back diffusion is

slow at ambient temperature but begins immediately at 40 °C. Longer immersion times result in an induction period. A model is proposed to explain differing kinetics for short and longer time HADD. The model posits different length scales comprising nanosurface (~ 10 nm) and mesosurface (1000 nm) for short and longer time HADD, respectively.

Experimental Section

Materials. PVC Tygon tubing (Fisher) was employed (O.D. 0.5 in, I.D. 0.25 in, wall thickness 3.2 mm. Reagent grade hexanes (95%), acetone (99.5%) and PVC powder were obtained from Sigma-Aldrich and used as received.

DEHP Content. Over ~5 years, experience revealed that DEHP plasticizer wt% varied significantly in Tygon tubing. For the present study, exhaustive extraction of DEHP was carried out with acetone. Upon immersion in acetone, samples swelled 3 or 4 times and acquired a cloudy appearance. Removal of nearly all DEHP required six successive 2 h immersions. DEHP accounted for ~45 wt %. Removal of DEHP was confirmed by the near absence of carbonyl absorption (ATR-IR) at 1700 - 1750 cm^{-1} . GC-MS was used to confirm the identity of DEHP. Based on measured DEHP content, samples used are designated PVC-45.

Sample Preparation. For each group of experiments, PVC-45 tubing was cut into the requisite number of 2 cm pieces, followed by cutting in half along the long tubing axis to provide pairs. So as to provide a convenient handhold, each piece was placed on a fishing hook (short of the barb for easy removal later) and labeled. Samples were dipped into fresh hexane (~ 30 mL, magnetic stirring) at 25 °C for selected times. After removal, the sample was immediately placed in contact with a Kimwipe so as to wick away excess solvent. Post-immersion sample pairs were

kept in plastic beakers. Hexane immersion time intervals were: 1, 2, 3, 5, 10, 15, 20, 25, 30, and 40 s; 1.5, 2, 3, 4, 5, 6, 7, and 8 min.

Attenuated Total Reflectance Infrared Spectroscopy. ATR-IR spectra were obtained with a Nicolet iS10 Smart-iTR equipped with standard germanium (Ge) or diamond (Dia) crystal attachments. The Smart-iTR attachment employs an operator independent standard pressure of ~40 psi on a sample that is held horizontally. This is achieved by placing the sample on the crystal platform and turning a knurled knob that pins the sample until a “click” is obtained. This pressure was used for every sample measurement.

A standard background was obtained before each sample measurement. Instrument software was used to obtain peak areas. Each data point (e.g., Figure 3A) is the average of six determinations from three measurements on two separately prepared samples. Instrument resolution was set to 4 cm^{-1} for all determinations, which is a typical value used for solids and liquids.

Spectra were obtained within 2 h after sample removal from hexane, although preliminary experiments at ambient temperature showed negligible change in ATR-IR peak areas for at least 24 h. Each spectrum was obtained with 8 scans in order to minimize acquisition time consistent with accuracy. By releasing and repositioning the sample, spectra from three areas were obtained. With three areas per sample and duplicate determinations, a total of six carbonyl peak areas were obtained for each immersion time.

To investigate whether heating affected peak areas during ATR-IR data acquisition, two samples were immersed in hexane for 1 min at $25\text{ }^{\circ}\text{C}$. Eleven spectra were obtained using 40 scans at 10 sec intervals without moving the sample. Peak areas remained constant within experimental error.

Mass loss was considered as a way to confirm results from ATR-IR and as a concern with regard to back diffusion from hexane solution. The wall thickness for PVC-45 is ~3 mm, while the maximum depletion zone is ~1 μm . That is, for the diamond crystal (d_p 1267 nm) a finite carbonyl intensity is still observed for the maximum immersion time of 6 min. For a typical sample mass of 1.2 g and assuming *complete* DEHP mass loss to a depth of 1 μm the calculated mass loss is $\sim 2.4 \times 10^{-4}$ g, which is too low for accurate measurements with a standard analytical balance.

Samples were dipped into hexane for periods of time from ~ 2 sec to 8 min. At the exposure times used, hexane must diffuse into the near surface, but no visual change in shape occurs. After up to 8 min exposure to hexane there was no detectible mass gain for the samples.

Diffusion path length. Using the Fickian model for diffusion requires estimation of the path length L . We assumed that the depth of penetration of IR radiation, d_p approximates L . Penetration depth d_p is sensitive to the refractive index of sample. For example, PVC-45 has a refractive index of 1.5157, and the calculated penetration depth is 1267 nm for diamond and 389 nm for Ge (Supplemental Information, page 8).

However, for a hypothetical sample with refractive index of 1.65, the calculated penetration depth increases to 2800 nm for diamond and 680 nm for Ge. Similar refractive indices for DEHP (1.48) and PVC (1.53) preclude significant changes in d_p due to refractive index as DEHP is removed from the outermost surface.

DEHP Diffusion from the bulk to the

Figure 1. A representative set of ATR-IR carbonyl peak areas for PVC-45 as a function of immersion time in hexane (Ge crystal).

mesosurface. The diffusion of DEHP from the bulk into the depleted mesosurface was also investigated using ATR-IR spectroscopy at 22 and 40 °C.

22 °C. Duplicate PVC-45 samples were immersed in hexane for 20 s. DEHP back diffusion was monitored by ATR-IR spectroscopy (3 spots per sample) at 0, 1, 2, 3, 4, 5, 7, 9, and 11 days. The same samples were used for Ge and Dia spectra. Duplicate samples were again prepared but the immersion time was 6 min. ATR-IR spectra were obtained for the same time intervals and 13, 15, 22, and 29 d.

40 °C. Duplicate samples were prepared as above. Separate sets of 20 s and 6 min samples were used for obtaining Ge and Dia crystal spectra. Time intervals for back diffusion in 20 s samples were 0, 1, 2, 3, 4, 6, 8, 24, 30, and 48 h. Time intervals for 6 min samples were 0, 2, 4, 8, 24, 26, 28, 30, 32, and 48 h.

XPS instrumentation and measurement. X-ray photoelectron spectroscopy was performed with a Thermo Scientific ESCALAB 250 spectrometer with a focused monochromatic Al K α X-ray (1486.6 eV) source and a spot size of ~500 μ m. Samples were mounted onto a sample holder with double-sided adhesive tape. To prevent outgassing from samples, the sample holder was cooled with flow of liquid nitrogen. The incident X-ray beam was 45° to the sample while the X-ray photoelectron detector was normal (TOA 45°). To achieve high signal-to-noise ratio a large area XL magnetic lens was used. Charge compensation was employed during data collection by using an internal flood gun (2 eV electrons) and a low energy Ar⁺ external flood gun. To have sufficient charge compensation, argon gas pressure was kept at $1 \cdot 10^{-8}$ mbar during the experiment. Constant analyzer energy (CAE) mode was utilized, with pass energy 20 eV for the detailed spectra, and 150 eV for the survey scans. The observed binding energies were correlated to the C 1s peak at 284.8 eV. Data analysis was performed with ThermoAvantage Ver.

4.84 software. For peak fitting the Gaussian-Lorentzian product function with L/G ratio 30% was used as a model function.

Results and Discussion

The findings described herein began with interest in a sodium sulfide surface treatment for plasticized PVC that was reported to thwart plasticizer leaching.[31] We failed to reproduce the reported surface modification. Trials designed as control experiments led to exploration of hexane assisted diethylhexylphthalate diffusion (HADD) from plasticized PVC (Tygon tubing). As described in the Experimental section, these samples are designated PVC-45 to indicate diethylhexylphthalate (DEHP) wt%.

Exposure of plasticized PVC to hydrocarbon solvents was previously reported to form a metastable, near-surface DEHP depletion zone.[15, 27-29] These and related studies involved analysis of DEHP in the solvent after immersion.[23, 24, 27, 28] We discuss below an ATR-IR method that provides direct measurement of early-stage DEHP near surface diffusion. This approach uses the DEHP carbonyl absorption, which occurs in a window for PVC and the metastable state obtained after immersion in hexane.

Vergnaud indicated hexane desorbs with difficulty from DEHP plasticized PVC, but immersion times were longer than those employed in the present investigation. From our experience, near-surface hexane volatilized rapidly along with extraction of DEHP and glass formation. Diffusion of DEHP from the bulk into the glassy near surface region is much slower

than HADD. With slow back diffusion after short immersion times (< 30 sec) and quenched diffusion after immersion times, spectra were conveniently obtained about an hour later.

ATR-IR spectra for PVC and PVC-45 are provided in Figure 1S. PVC has negligible absorbance at $\sim 1715\text{ cm}^{-1}$, [12] while rapid solvent volatilization and slow DEHP diffusion from the bulk allow accurate measurements of carbonyl peak areas as a function of immersion time. ATR-IR spectroscopy thus proved to be a facile method for the determination of the relative concentration of DEHP remaining after immersion in hexane. Germanium and diamond (Dia) crystals were used to acquire ATR-IR spectra.

The depth of penetration (d_p) for the evanescent wave at 1715 cm^{-1} ($\lambda = 5831\text{ nm}$) is 389 nm for Ge and 1270 nm for Dia. Figure 1 shows a representative set of ATR-IR carbonyl

peak areas as a function of immersion time using a Ge crystal. Using integral peak areas directly from the ATR-IR instrument, a typical zero time peak area was 0.75 decreasing to ~ 0.25 after 8 min. Area attenuation was modeled after Fick's second law, which is discussed briefly below.

Fickian Model. Figure 2 depicts a homogenous slab with a molecular species diffusing from the near surface. This model is used for HADD as swelling by hexane is slight and

ephemeral due to high volatility.[26] Fick's second law is given by Eq 1 where c is the concentration (g/cm^3), t is time, D is the diffusion coefficient (e.g., cm^2s^{-1}),

$$\frac{\partial c}{\partial t} = D \frac{\partial^2 c}{\partial x^2} \quad \text{Eq. 1}$$

and x is position (cm). The derivation of the relationship for HADD in Supplemental Information follows prior investigations for release of a small molecule from a polymeric solid such as drug release from a matrix polymer.[26, 32-37] Eq 2 follows from Fick's second law,

$$\frac{A_o - A_t}{A_o} = 2 \left(\frac{D}{\pi 2L} \right)^{\frac{1}{2}} t^{\frac{1}{2}} \quad \text{Eq 2}$$

where A_o is the carbonyl peak area for PVC-45, A_t is the peak area after immersion in hexane for time t , D is the diffusion coefficient in cm^2/s and L is the diffusion path length in cm.

Previous solvent assisted diffusion studies were based on analysis of DEHP in the extraction solvent and used slab thickness or other estimate.[15, 23, 24, 27-29] Herein, the diffusion path length L is defined as the depth of penetration of the evanescent wave. This depth is dependent on wavelength, angle of incidence, refractive index of the medium encountered by the evanescent wave and the ATR-IR crystal employed (Supplemental Information). Equation 2 leads to an expression for the diffusion constant D from the slope of $A_o - A_t/A_o$ vs. $t^{1/2}$ (Eq 3).

$$D = \frac{\pi(\text{slope})^2 L^2}{4} \quad \text{Eq 3}$$

HADD. Figure 3A shows a representative data set of absorbance vs. time using a Ge crystal. As noted in the Experimental section, each data point is the average of six determinations from three measurements on two separately prepared samples. Upon immersion in hexane, rapid attenuation for absorbance is seen in Figures 1 and 3A. Following Eq 2, a graph of $(A_0 - A_t)/A_0$ vs. $t^{1/2}$ is shown in Figure 3B. Interestingly, the diffusion process is separable into two time regimes, viz. $< \sim 30$ sec and > 30 sec but $< \sim 8$ min. There is a region of nonlinearity between ~ 25 and 30 sec as diffusion rapidly attenuates.

A similar set of experiments was carried out using a Dia crystal. Absorbance vs. time of immersion in hexane is available in Supplemental Information (Figure S2). Figure 4 shows $(A_0 - A_t)/A_0$ vs. $t^{1/2}$ for HADD from Dia crystal data with linear fits for < 30 sec and from > 30 sec to ~ 8 min.

Table 1. Diffusion coefficients for HADD

The determinant for D is the slope of $(A_0 - A_t)/A_0$ vs. $t^{1/2}$ (Eq 3). From Figures 3 and 4 slopes for $(A_0 - A_t)/A_0$ vs.

Time	Crystal	Slope $(A_0 - A_t)/A_0$ vs. $t^{1/2}$	$d_p(\text{nm})$	$D_{t,c} (\text{cm}^2/\text{s})$
< 30 s	Ge	0.076	389	7.4×10^{-12}
	Dia	0.065	1267	5.7×10^{-11}
$30 \text{ s} < t < 8 \text{ min}$	Ge	0.012	389	1.2×10^{-13}
	Dia	0.013	1267	1.5×10^{-12}

$t^{1/2}$ are listed in Table 1. Slopes for < 30 sec are 0.076 (Ge) and 0.065 (Dia). For $30 \text{ sec} < t < 8 \text{ min}$ slopes are 0.012 (Ge) and 0.013 (Dia). The higher slope for $t < 30$ sec using the Ge crystal may be understood in terms of a model shown in Figure 5 that ignores nonlinear attenuation

of infrared radiation with depth. For HADD at short time (< 30 sec) hypothetical DEHP

depletion is shown. The fraction depletion is $\sim 0.3 d_p$ for Ge estimated as $\sim 117 \text{ nm}$ ($389 \text{ nm} \times 0.3$). This level of depletion is 30% for Ge, but $\sim 10\%$ for Dia due to the greater depth of penetration of IR radiation. By this reasoning, the greater slope for the Ge crystal compared to Dia is accounted for by $A_o - A_t$ being greater for Ge at any time $t_x < 30 \text{ sec}$. On the other hand for $t > 30 \text{ sec}$ the slopes for Ge and Dia crystals are the same within experimental error.

Based on rapid diffusion or extraction of DEHP by hexane at $t < 30 \text{ sec}$, it appears that hexane is soluble in the plasticized surface. That is, hexane is soluble in the blend of PVC and DEHP and DEHP rapidly diffuses into hexane driven by entropic considerations. However, hexane has a very low solubility in PVC so that within 30 sec a near surface PVC domain forms a nanobarrier. That is, diffusion of hexane into PVC is much slower than diffusion into plasticized PVC, which in turn slows the out-diffusion of DEHP. That is HADD is slowed due to the formation of a glassy PVC near surface domain that acts as a barrier to in-diffusion of hexane and out-diffusion of DEHP. The change in slope for $(A_o - A_t)/A_o$ vs. $t^{1/2}$ occurs at 30 s independent of ATR-IR crystal. That is, even though d_p for Dia is 3.3 times greater than Ge, the time at which the nanobarrier forms is constant. The nanobarrier effectively “shuts the door” *in situ* to rapid HADD.

Diffusion coefficients.

Diffusion constants for HADD were calculated using Eq 3. As noted

above, L was defined as the depth of penetration of the evanescent wave for Ge and Dia was defined as d_p (Table 1, Supplemental Information). Diffusion constants are designated $D_{t,c}$, where t is one of two time segments (“30” for less than 30 sec, “8” for $30 \text{ sec} < t < 8 \text{ min}$) and c is the ATR-IR crystal. Accordingly, $D_{30,Ge}$ is $7.44 \times 10^{-12} \text{ cm}^2/\text{s}$ (Table 1). The respective slopes for $(A_o - A_t)/A_o$ are similar, but the ratio of $(d_{p,Dia})^2 / (d_{p,Ge})^2$ is 10.6 and accounts for the factor of ~ 10 in diffusion coefficients.

Different experimental conditions preclude quantitative comparisons with Taverdet’s studies of DEHP diffusion. For example, one study immersed PVC-50 into heptane for time periods of 2, 4, 16, 25, and 36 min. This was followed by “drying” at 100°C for 5 min and re-immersion to assess the time lag for solvent assisted diffusion.[38] While quantitative comparisons are not possible, our results generally agree with Taverdet in that longer immersion in hexane results in longer lag times for back diffusion.

Diffusion of DEHP into DEHP depleted PVC. Samples immersed in hexane for 20 s (within the $< 30 \text{ s}$ time regime) and 6 min were monitored for recovery of the DEHP carbonyl absorbance due to back diffusion into the DEHP depleted domain from the “bulk”, which is a depth greater than the respective d_p ’s.

PVC-45 has a wall thickness of $> 3 \text{ mm}$ or $3000 \mu\text{m}$ so that back diffusion studied by ATR-IR involves the mesosurface, which is defined as $\sim 10 - 1000 \text{ nm}$.

Figure 6 shows the fraction of carbonyl peak area (A_t/A_o , Ge) as a function of time t at 23°C . For sample A,

which was immersed in hexane for 20 s, the peak area increases to ~90% of that for PVC-45 in 2-3 d and then slowly reaches the absorbance for as-received PVC-45 in 9 - 12 d.

Peak area recovery for PVC-45 immersed in in hexane for 6 min is sample dependent. B1, B2 and C1, C2 were duplicates. B1, B2 and C1 have 9-12 d induction periods, then a “breakthrough” followed by slower back diffusion. C2 shows decreasing A_t/A_o over ~ 13 d followed by slow recovery. After 30 d, absorbance for B1, B2 and C1 has recovered to ~80% A_o but C2 is at ~30% PVC-45.

Figure 7 provides A_t/A_o (Ge) vs. t at 40 °C for samples previously immersed in hexane for 20 sec and 6 min, respectively. Peak area recovery is much faster at 40 °C than 23 °C. The sample immersed for 20 sec shows a high carbonyl peak area after only 12 hr and complete recovery in 24 hr. Samples immersed in hexane for 6 min show an induction period of ~12 hr, a sluggish increase in absorbance and incomplete recovery at 48 hr. The slow back diffusion of DEHP is attributed to formation of a glassy PVC meso-domain acting as a barrier, which is discussed further below.

In Supplemental Information, figures paralleling Figure 6 (Figure S2) and Figure 7 (Figure S3) are provided for a study of back diffusion with a Dia crystal at 23 and 40 °C. The rates of change are similar to those obtained with Ge. For example, after immersion for 6 min, the induction period at 23 °C before back diffusion is about 9 days

(Figure S2). At 40 °C back diffusion is faster (Figure S4). The induction period for PVC-45 previously immersed in hexane for 6 min is barely resolved (~ 1 d).

Figure S3 shows a graph of $(A_o - A_t)/A_o$ vs. $t^{1/2}$ for back diffusion at 23 °C (Figure S2). Figure S5 shows a similar graph for 40 °C / using the Dia crystal (Figure S4). Processes involved in near surface re-plasticization include formation of an interfacial zone as DEHP diffusion begins, swelling, and a change in state from a mesosurface glass to a gel like solid. The mesosurface glass must have a T_g considerably greater than 25 °C, while PVC-45 has a T_g of -52 °C. This change in state accounts for the slow kinetics. The multiple processes preclude a simple analysis, but an analysis below from fast-recovery trend lines gives some interesting insights.

Quantifying Back Diffusion. The slope of (A_t/A_o) vs. $t^{1/2}$ was obtained in the fast recovery period, which is defined as the nearly linear segments of (A_t/A_o) vs. $t^{1/2}$ curves highlighted in Figure 8 for B1. The same analysis for C1 is shown in (Figure S8). Coefficients for DEHP back diffusion using Ge and Dia crystal were calculated by using Eq. 3 in an analogous fashion to that for HADD. Samples B1 and C1 were selected due to consistent results from peak areas.

Variables and calculated DEHP back diffusion coefficients (D_b) are summarized in Table 2. Compared to HADD, coefficients for back diffusion are 2 – 3 orders of magnitude lower since no solvent is involved. Again, while the respective slopes for (A_t/A_o) vs $t^{1/2}$ are similar, the back diffusion coefficient for DEHP for Ge was ~ 10 times lower than that for Dia crystal due to the difference between $d_{p,Dia}$ and $d_{p,Ge}$. Consequently, the calculated coefficients for DEHP back diffusion are relative values based on d_p for ATR-IR crystals.

The difference between $d_{p,Dia}$ and $d_{p,Ge}$ provides an opportunity to calculate the DEHP

Table 2. Coefficient of DEHP back diffusion in PVC.

Sample	Crystal	Fast recovery period	Slope A_t/A_o vs. $t^{1/2}$	d_p (nm)	D_b (cm ² /s)
B1	Ge	Day 7 - Day 17	0.0014	389	2.3×10^{-15}
	Dia		0.001	1267	1.3×10^{-14}
C1	Ge	Day 9 - Day 17	0.0018	389	3.9×10^{-15}
	Dia		0.0013	1267	2.1×10^{-14}

diffusion coefficient in the glassy PVC mesosurface. As shown in Figure 9A, the slope of (A_t/A_o) vs. t starts to increase at point A (day 5) for the Dia crystal, suggesting that DEHP back diffusion flow has reached the boundary of Dia crystal penetration depth (1267 nm). This hypothesis is illustrated in Figure 9B. Similarly, the slope of (A_t/A_o) vs. t starts to increase at point B (day 7) for the Ge crystal consistent with DEHP back diffusion flow reaching the boundary of Ge crystal penetration depth (389 nm) at day 7 (Figure 9C). An analogous result was obtained for sample C1 (Figure S9). For C1 the

Dia crystal increase was observed at day 7 while the Ge crystal increase occurred at day 9.

For samples B1 and C1, the increase in absorbance due to DEHP back diffusion consistently occurred for the Dia crystal two days before the Ge

crystal. This may be taken to indicate that the front of DEHP back diffusion flow took 2 days to diffuse from the boundary of Dia crystal penetration depth (1267 nm) to Ge crystal penetration depth (389 nm). In 1905, Einstein developed Eq. 4 to calculate diffusion path length from diffusion coefficient and time.[39]

$$\lambda = \sqrt{2Dt} \quad \text{Eq. 4}$$

where λ is diffusion path length, D is diffusion coefficient and t is time. Eq. 5 is derived from Eq. 4.

$$D_b = \frac{(d_{p,Dia} - d_{p,Ge})^2}{2(t_{Ge} - t_{Dia})} \quad \text{Eq. 5}$$

where D_b is the coefficient of DEHP back diffusion, $d_{p,Dia}$ and $d_{p,Ge}$ are the respective penetration depths of Dia and Ge crystals, t_{Ge} and t_{Dia} are the times to obtain the first data points from which the slopes of (A_t/A_o) vs. t curves for Ge and Dia crystal start to increase.

The difference between t_{Ge} and t_{Dia} is 2 days for both sample B1 and C1. According to Eq. 5, the coefficients of DEHP back diffusion for samples B1 and C1 are both $2.2 \times 10^{-14} \text{ cm}^2/\text{s}$. This result is close to D_b calculated using Eq. 3 for Dia crystal, but 10 times higher than that for Ge crystal. This is the first time that diffusion path length and diffusion time are directly observed by

Figure 10. Survey XPS spectra of PVC-45: **A**, as-received; **B**, after immersion in hexane (6 min).

experiment and diffusion coefficients are calculated accordingly.

For back diffusion, a change of state occurs from a glass ($T_g > 25\text{ }^{\circ}\text{C}$) back to a tough rubber ($T_g - 52\text{ }^{\circ}\text{C}$). Usually diffusion is not accompanied by a change in state. Accordingly, diffusion coefficients are much higher. In 2009, McWatters studied the diffusion of several volatile organic compounds (benzene, toluene, ethylbenzene and xylenes) through a 0.76 mm thick flexible PVC membrane. Diffusion coefficients for these molecules were found in the range of 5.0×10^{-9} to $9.0 \times 10^{-9}\text{ cm}^2/\text{s}$, which are higher than our result by 4 to 5 orders of magnitude.[40] This difference is attributed to re-plasticization of the glassy PVC mesosurface ($T_g > 25\text{ }^{\circ}\text{C}$) followed by diffusion rather than diffusion through “flexible PVC”, which has an unspecified plasticizer content.

X-ray Photoelectron Spectroscopy. XPS was employed for chemical analysis to determine the concentration of DEHP in the outermost surface ($\sim 3\text{-}5\text{ nm}$) that we designate the nanosurface. Spectra were taken at $\sim -186\text{ }^{\circ}\text{C}$ to avoid volatilization of DEHP in ultra-high vacuum. Perhaps cooling attenuates decomposition previously observed for PVC[41] as no attenuation of the C/Cl ratio was seen in successive runs.

Figure 10A shows a survey XPS spectrum for PVC-45. The O(1s) peak at 532.6 eV is unique for DEHP and confirms its presence in the nanosurface. Cl (2s) and Cl(2p) peaks for PVC are at 200.0 and 201.6 eV, respectively. Atom % and atom ratios from survey spectra for PVC-45 are listed in Table 3. PVC-45 immersed in hexane for 6 min was chosen for comparison, as this immersion time corresponds to the DEHP near surface depletion zone. Calculated atom % and atom ratios are shown for PVC-45 and PVC.

The carbon atom% for PVC-45 is close to the calculated value but O is high and Cl low. High oxygen and low Cl may be due in part to a preferred orientation of alkyl chains and concentration of DEHP at the outermost surface or the presence of processing aids. After immersion in hexane for 6 min the carbon atom% drops while Cl increases dramatically from 9.56 to 28.5 atom%. Oxygen is reduced from 11.5 to 2.9 atom%. The C/Cl atom% ratio decreases from 8.26 for PVC-45 to 2.39 which approaches that for PVC (2.0). Overall, the changes in C, Cl and O atom% are consistent with removal of DEHP from the nanosurface.

Table 3. XPS atom % and atom ratios from survey spectra for PVC-45 and a sample immersed in hexane for 6 min.

PVC-45	C		Cl(2p)		O		C/Cl		O/Cl		C/O	
	Obs	Calc	Obs	Calc	Obs	Calc	Obs	Calc	Obs	Calc	Obs	Calc
	79.7	78.1	10.4	15.0	9.93	6.9	7.76	5.21	0.95	0.46	8.03	11.76
6 min ^{a,b}	68.3	67	28.3	33	3.4	0	2.39	2	0.11	0	21.1	-

a. PVC-45 after immersion in hexane for 6 min.

b. Calculated values for PVC.

High resolution spectra for C(1s), O(1s) and Cl(2p) are shown in Figure 11. For PVC-45 C(1s) peaks at 288.7 and 286.5 eV are assigned to the DEHP carbonyl carbon ($\text{O}=\underline{\text{C}}-\text{O}$) and ester carbon ($-\text{O}-\underline{\text{C}}-\text{C}$), respectively. Although DEHP is a molecular species and has not been characterized by XPS, the chemical environment for the ester group is similar to poly(ethylene terephthalate) or PET resulting in comparable binding energies.[42-44]

O(1s) binding energies for PVC-45 occur at 533.3 and 531.9 eV, respectively (Figure 11B). These binding energies are also similar to ester and carbonyl oxygen peaks observed for PET.[42-46] The Cl(2p) peak for PVC-45 has two components, Cl(2p_{3/2}) at 200.0 eV and Cl(2p_{1/2}) at 201.6. As found previously, the separation energy is ~1.6 eV while the peak intensity ratio for Cl(2p_{3/2}) / Cl(2p_{1/2}) is 2:1.[47, 48]

After 6 min immersion in hexane the DEHP C(1s) carbonyl peak at 288.7 eV is absent (Figure 11A). The resulting spectrum simplifies to two C(1s) peaks at 284.8 and 285.7 eV that are assigned to $\underline{\text{CH}}_2$ and $\underline{\text{C}}\text{-Cl}$. These peaks are of equal intensity and indistinguishable from previous reports for PVC[41, 49-51] and provides support for the absence of DEHP in the nanosurface.

The Cl(2p) peak greatly intensifies and is identical to previous reports for PVC noted above.[47, 48] The O(1s) peak changes to a broad, low intensity peak at 532.4 eV, which is likely due to residual processing aids.

Figure 11. High resolution XPS spectra for A, C(1s), B, O(1s) and C, Cl(2p).

Conclusion

The present study focuses on plasticized PVC and the direct measurement of near surface hexane assisted DEHP diffusion (HADD). Hexane effects near surface diffusion of diethylhexylphthalate and acts as a surrogate lipophilic medium. DEHP is highly soluble in hexane providing an entropic driving force for extraction / diffusion. An IR window for PVC from 1500 - 1900 cm^{-1} enabled direct measurement of HADD by ATR-IR by monitoring the DEHP carbonyl absorption at 1715 cm^{-1} . Hexane must have a transient presence in the outermost surface during DEHP diffusion.

However, hexane is highly volatile and no trace is observed in any ATR-IR spectra. Rapid hexane volatilization accompanied by a change in state from an elastomer (T_g -52 °C) to a glass (T_g > 25 °C) quenches back diffusion. As a result, attenuated C=O peak areas were “frozen” for convenient acquisition. The 70% decreases in

Figure 12. A, PVC-45; B, Time < 30 sec; C, Time > 30 sec and < 8 min.

initial C=O peak area after 8 min immersion permitted good accuracy in peak area measurements.

As illustrated in Figure 12A-B, HADD is fast for short times (< 30 s) but slower for longer immersion (Figure A-C, $30 \text{ s} < t < 8 \text{ min}$). Figure 12B represents the surface composition after HADD for < 30 sec immersion. During this time, HADD results in an increasing layer

thickness of glassy PVC and an accompanying increase in mesosurface T_g . The relatively high diffusion rates (Table 1, 10^{-11} to 10^{-12} cm²sec⁻¹) are depicted by large arrows for DEHP extraction and hexane diffusion into the near surface. HADD diffusion coefficients for short time immersions are 6 times higher for Ge and 4 times higher for Dia compared to corresponding values for longer immersion (Table 1). Because the diffusion path length L was chosen for the depth of penetration of the evanescent wave HADD diffusion coefficients for Ge are ~10 times smaller than those for Dia due to the relationship $(d_{p,Dia})^2 / (d_{p,Ge})^2$ (Eq 3).

Hexane immersion and diffusion of DEHP results in a physical change in the topmost mesosurface from elastomeric (T_g -52 °C) to glassy (T_g > 25 °C) , which is phenomenologically similar to reduced dimensions for thermoresponsive hydrogels.[52] That is, hexane extraction of DEHP depicted in Figure 12A- B results in a near surface LCST-like transition, which brings about a > 97% reduction in the rate of DEHP diffusion compared with longer immersion times. Even though d_p for Dia is 3.3 times greater than Ge, the time at which the nanobarrier forms is constant. Thus the nanobarrier “shuts the door” *in situ* to rapid HADD.

Once the surface is depleted of plasticizer, the nanosurface solubility of hexane decreases substantially as hexane has low solubility in PVC.[53] A synergistic increase in mesosurface T_g toward that of PVC coupled with low solubility of hexane in PVC accounts for the decreased DEHP diffusion rates upon longer hexane immersion. The formation of a “membrane glass”[38] is depicted in Figure 12C. In view of the relatively rapid formation of the glassy state, considerable heterogeneity may result. Heterogeneity in the polystyrene glassy state as a function of thermal history resulted in “spatially heterogeneous dynamics”.[54] Siretanu also found a heterogeneous polystyrene surface after exposure to aqueous electrolytes.[55] Although

high accuracy was obtained overall, rapid formation of the mesoglass may contribute to area-to-area and sample to sample variations in ATR-IR measurements.

It is possible that PVC vitrification is accompanied by crystallization. The extent of crystallinity in PVC has been controversial.[56] An estimate of $\sim 20\%$ by solid state ^1H -NMR avoids difficulties associated with thermal methods, particularly DSC.[57] If crystallization occurs, another barrier would arise that could account for long lag times for back diffusion. Whether or not crystallinity develops during HADD is unknown, but heterogeneous nucleation might account in part for the sample dependent recovery rates (Figure 6).

For a sample that was immersed in hexane for 20 s, back diffusion of DEHP at ambient temperature occurred within 24 h (Figure 12B-A). Processes involved in near surface re-plasticization include formation of an interfacial zone as DEHP diffusion begins, swelling, and a change from a mesosurface glass to a gel like solid. This multi-step process results in an induction period for DEHP back diffusion. The induction period is shorter for short hexane immersion (Figure 12B-A) compared to longer immersion (Figure 12C-A).

Coefficients for DEHP back diffusion using Ge and Dia crystal were calculated using the slope of (A_t/A_o) vs. $t^{1/2}$ in the fast recovery period along with Eq. 3. Compared to HADD, coefficients for back diffusion are 2 – 3 orders of magnitude lower due to the multiple processes noted above. The low back diffusion coefficients (10^{-14} - 10^{-15} $\text{cm}^2\text{sec}^{-1}$) are six – seven orders of magnitude slower than typical diffusion processes for gas separation membranes.[58]

In most cases, after an induction period, an onset for back diffusion was observed (Figures 8, 9). Rather than a diffuse process, this onset suggests a coherent interphase moves toward the surface. A systematic difference between the initiation time for back diffusion using Ge and Dia crystals was used to estimate back diffusion coefficients, (D_b). The same result was

obtained for both crystals ($2.2 \times 10^{-14} \text{ cm}^2/\text{s}$). D_b estimated by this novel method was close to that calculated using Eq. 3 for Dia but 10 times higher than that for Ge. Again, the penetration depth of Dia ($d_{p,\text{Dia}}$) and Ge ($d_{p,\text{Ge}}$) was used to approximate the diffusion path length L in the calculation of D_b using Eq. 3. Again, since similar slopes for (A_t/A_o) vs. $t^{1/2}$ were obtained for Dia and Ge crystals (Table 2), D_b is determined by $d_{p,\text{Dia}}$ and $d_{p,\text{Ge}}$. However $d_{p,\text{Dia}}$ and $d_{p,\text{Ge}}$ may not accurately represent the true back diffusion L , which is the DEHP depletion depth when back diffusion begins. On the other hand, this novel method provides an approach to calculate D_b without knowing the true value of L , which is hard to measure. Thus D_b calculated using this method seems to be a good estimate for the true value of D_b . Due to the fact that D_b estimated by this method was close to that calculated using Eq. 3 for Dia, $d_{p,\text{Dia}}$ appears close to the true diffusion path length L of DEHP.

X-ray photoelectron spectroscopy at liquid nitrogen temperatures provided nanosurface composition in agreement for PVC plasticized with 45 wt% diethylhexylphthalate. Survey and high resolution analysis after 6 min HADD revealed spectra similar to PVC, with DEHP absent from the nanosurface (Figure 11A depicted in Figure 12C).

In summary, ATR-IR coupled with XPS analysis has revealed details about the PVC-45 nanosurface and mesosurface accompanying HADD and back diffusion of the plasticizer DEHP. A similar approach may be applicable to other systems with plasticizers that have carbonyl functionality. In addition, a novel method to estimate a back diffusion coefficient D_b by using a systematic difference between the initiation time for back diffusion of Ge and Dia crystals was developed. This approach avoids the difficulty of knowing the actual diffusion path length L for DEHP.

Associated content

ATR-IR spectra for PVC and PVC-45 and spectra obtained with a diamond ATR-IR crystal are provided as well as calculations and derivations noted in the text.

Author information

*E-mail kjwynne@vcu.edu; Phone 804-828-9303; Fax 804-828-3846 (KJW)

Notes

The authors declare no competing financial interest.

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