Vapor-phase migration of DiBP and DBP through barrier-coated paperboard: Correlation between a permeation test method and simulated migration

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ABSTRACT: The aim of the study was to construct a correlation between a permeation test method that simulates the migration of organic vapors and the actual migration of chemical contaminants from barrier-coated paperboard packaging. A correlation of this nature would enable manufacturers of barrier-coated paperboard to estimate the barrier properties of paperboard on a quality control level. A direct correlation was not plausible because the migration mechanisms that apply to the permeation test method and the actual migration differ. However, an indirect correlation was established. The permeation test method gave an indication of film integrity, whereas the actual migration was found to be rather dependent on coating weight. The spiking method, testing temperature, and vapor pressure of the contaminants were found to be variables directly affecting the validity of the correlation between permeation and migration methods.

Application: This correlation will enable manufacturers of coated paperboard products to estimate the barrier properties toward di-n-butyl phthalate (DBP) and di-iso-butyl phthalate (DiBP) on a quality control level.

Paperboard is a lightweight material that can easily be cut and formed. It has relatively good durability, which makes it advantageous for use in the packaging industry. In contrast to other types of packaging materials, paperboard is made from a renewable material. Paperboard can also be recycled up to seven times, and modern paperboard manufacturing processes operate on a closed-loop system, requiring minimal external energy input [1]. Every day we benefit from products such as pharmaceuticals, dry foods, and fast foods that are packaged in paperboard.

The increased use of recycled fiber in the production of paperboard packaging materials has prompted the food packaging industry to investigate the suitability of recycled paperboard for use in food packaging applications. The recycled fiber may come from various materials, including newsprint, corrugated containers, cartons, etc. Consequently, the possible sources of contamination (e.g., printing inks, adhesives, waxes, fluorescent whitening agents, sizing agents, and biocides) are vast. Chemical contaminants present in the recycled paperboard may migrate from the paperboard into the food, thereby constituting a health concern for consumers.

To protect consumers, regulatory bodies may impose stringent rules on packaging materials, with specific migration limits (SML) set for a vast range of potentially hazardous chemicals that might be present in recycled paperboard [2-4]. The most effective strategy proposed to impede the migration of chemical contaminants is the use of functional barriers, either in the form of an inner liner or as a barrier coating on the inner side of the paperboard.

MECHANISMS OF PENETRANT TRANSFER THROUGH THIN POLYMER FILMS

In a comprehensive review, Chatham [5] described the movement of penetrant molecules through thin barrier films applied to a polymer surface to occur by two mechanisms. The dependency of the penetrant transmission rate on the coating thickness is very different for the two mechanisms, as evaluated in terms of permeability of noncondensible gases such as oxygen. The mechanisms described below may differ slightly when applied to condensable vapors, such as water and organic vapors, because of the increased interaction that might occur between the penetrant, substrate, and barrier film.

Diffusive flow by the solution-diffusion mechanism

The diffusive flow of a penetrant, *i*, through the substrate and the barrier film is described by:

$$\frac{1}{\rho_{i,T}} = \frac{\tau_T}{P_{i,T}} = \frac{\tau_s}{P_{i,s}} + \frac{\tau_c}{P_{i,c}} \quad (1)$$

where $\rho_{i,T}$ is the total permeation rate of penetrant, $P_{i,T}$ is the apparent permeability of the penetrant in the whole struc-

ture, τ_T is the total thickness ($\tau_s + \tau_c$), and $P_{i,s}$ and $P_{i,c}$ are the permeabilities of the penetrant in the substrate and the coating, respectively. Therefore, according to this mechanism, the total permeation rate of the penetrant should decrease as the thickness of the barrier film is increased [5].

Flow through defects such as pinholes (defect model)

Prins and Hermans [5,6] developed an expression for the flux, F_i, of a penetrant, i, through defects such as pinholes in a metalized polymer. The steady state diffusion equation was applied to obtain Eq. (2):

$$F_i \approx \frac{D_i}{\tau_s}(c_o - c_1)\Theta(1 + 1.18\lambda) \quad (2)$$

where D_i is the diffusion coefficient of the penetrant in the polymer, τ_s is the polymer thickness, Θ is the fraction of the surface left uncovered by the defects, c_o and c_1 are the concentrations of the penetrant on either side of the barrier film, and λ is the ratio of the film thickness to the radii of the defects. This mechanism predicts that the flux is independent of the barrier film thickness [5].

ASSESSING THE EFFICIENCY OF FUNCTIONAL BARRIER COATINGS TO PREVENT MIGRATION

The efficacy of functional barriers can be assessed using a conventional migration test. It involves the use of a food simulant and the subsequent quantification of the migrant by chromatographic techniques. The migration test involves placing the paperboard in contact with a suitable food simulant for a specific period and at a specific temperature. Thereafter, the food simulant is extracted with a suitable solvent and the extract analyzed by chromatographic techniques to determine the concentration of the chemical contaminants that have migrated from the paperboard into the food simulant. Drawbacks are that the migration test is time consuming and the chromatographic equipment required for quantification of SMLs are very costly and require a high level of operator expertise. Because of the complexity of this process, implementation of migration testing at quality control level during the manufacture of paperboard is not a practical option.

A simplified permeation test method developed by Tiggelman et al. [7] that simulates the general migration behavior of organic vapors through functional barriers can be used as an indication of barrier efficiency. The permeation method, defined by the heptane vapor transmission rate (HVTR), is a simple, rapid method that can be used in a quality control laboratory with minimal startup costs and with a low level of operator expertise. The method is based on the mass pickup of a suitable absorbent after being exposed to a saturated heptane environment for a predefined period. To date, results from the permeation method and actual migration levels of specific contaminants have yet to be correlated.

This study aims to determine whether a correlation can be established between the permeation method and the actual migration levels of specific chemical contaminants. Such a correlation, if used for quality control during paperboard production, would allow paperboard manufacturers to estimate the barrier property efficacy of coated paperboard to di-n-butyl phthalate (DBP) and di-isobutyl phthalate (DiBP).

EXPERIMENTAL

Sample preparation

Calibration standards

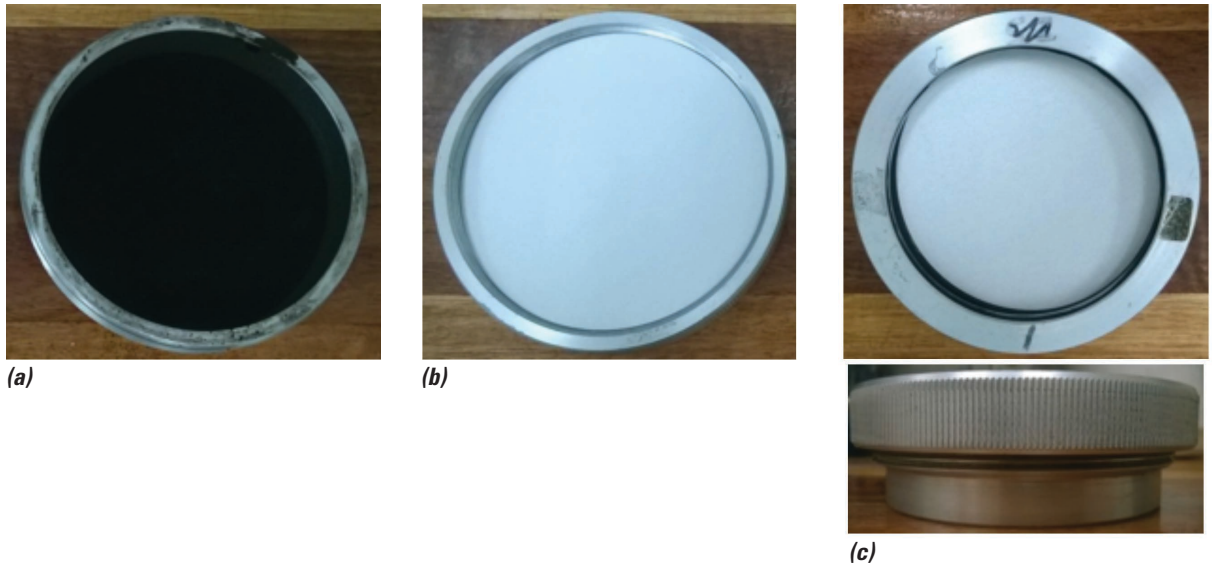
DBP, DiBP, and bis(2-ethylhexyl) phthalate (DEHP) with a purity of 99% were supplied by Sigma-Aldrich (St. Louis, MO, USA). The calibration standards were made up in HPLC-grade acetone. The internal standard, di-butyl phthalate-3,4,5,6-d_4 (d-DBP) with a purity of 98%, was supplied by Sigma-Aldrich. The calibration standards were prepared in 10 mL volumetric flasks with the concentration varying from 2.0-1250 μg in 10 mL. This was used as the quantification range. The calibration curve was constructed by plotting the response ratio of the analyte peak to the internal standard peak against the mass of analyte in the 10 mL volumetric flask. The internal standard was prepared as a 100 ppm solution in acetone. For this study, 25 µL of the internal standard was added to each of the calibration standards as well as the unknown samples.

Barrier-coated paperboard

A polyvinylidene chloride (PVDC) barrier coating (Ixan and Diofan A 297, Solvay; Brussels, Belgium) was used, and applied to the paperboard as one-layer and two-layer coating configurations. A custom-built K Control Coater (Scientific Manufacturing Cc; Milnerton, South Africa) was used to apply the barrier coatings to the 350 g/m^2 paperboard substrate manufactured from recycled fiber. The thickness of the applied film was varied to produce samples of varying barrier efficiency using standard K101 close wound metering bars (nos. 1, 2, 3, and 7) and a smooth metering rod. To vary the pinhole density of the coating, the PVDC barrier polymer was subjected to a shear rate of 1300 rpm for 0, 1, 5, 7, and 10 min to incorporate air into the barrier polymer. The coating was applied to the paperboard surface as a single-layer configuration using the no. 7 coating rod and allowed to dry. When dry, pinholes formed on rupture of the air bubbles.

Sample spiking with model contaminants

The principle of the spiking method used by Poças et al. [8] was used for the migration tests performed at 60°C for 24 h. The spiking solution was composed of an equal volume of DBP (2500 ppm), DiBP (2500 ppm), and DEHP (2500 ppm). Blotting paper discs with an area of 0.2 dm^2 were placed on a clean, dry watch glass and 1.3 mL of the spiking solution was applied to the blotting paper surface and left to dry for 25 min. To spike the paperboard sample with an area of 0.2 dm^2, the spiked blotting paper disc was placed in contact



1. Heptane vapor transmission rate (HVTR) cell setup.

with the non-barrier side of the paperboard, wrapped in aluminum foil, and stored at 60°C for 24 h. Thereafter, the paperboard sample was removed and used for the migration analysis. The concentrations of the model compounds present in the blotting paper and in the paperboard after 24 h contact with the blotting paper were confirmed by direct extraction in acetone and analysis of the extract by gas chromatography–mass spectrometry (GC-MS).

Permeation test - heptane vapor transmission rate

The base of an aluminum permeation cell containing 4-7 g activated carbon (**Fig. 1**) was weighed and the mass noted, W_1. The coated paperboard substrate was placed into the lid of the cell and fastened to the base of the cell with the coated side of the substrate facing outward. The cell was placed in a desiccator saturated with heptane vapor (23°C) and exposed for 3 h. After the exposure time had elapsed, the cell was removed from the desiccator. The lid of the aluminum cell was removed and the base of the cell weighed, W_2. The mass uptake of the activated carbon due to exposure to the saturated heptane environment was used to calculate the HVTR using Eq. (3):

$$\mathrm{HVTR}(g/m^2/h) = \frac{W_2 - W_1}{A. \times t} \qquad (3)$$

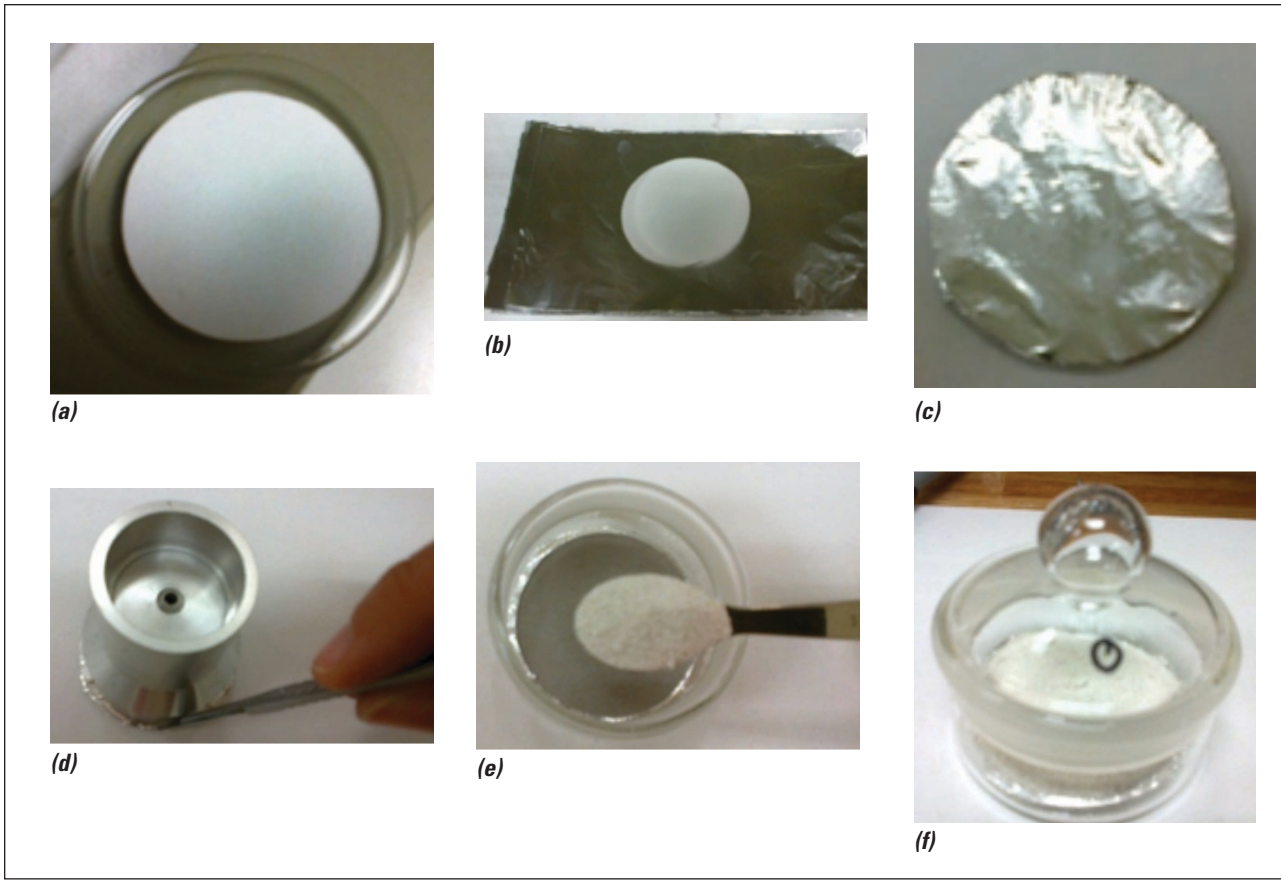
where *HVTR* is the heptane vapor transmission rate in $g/m^2/h$, W_1 and W_2 are the mass of the cell before and after exposure to the saturated heptane vapor respectively in *g*, *A* is the exposed sample area in m^2, and *t* is the time of exposure in *h*. Results were based on duplicate measurements because of availability of sample material.

Migration tests

A weighing bottle with a fitted lid, having a diameter of 55 mm and a depth of 30 mm, was used as an immersion cell. A strip of foil (65 mm wide and 200 mm long) was cut and the paperboard sample (52 mm diameter) was placed onto the foil, with the barrier-coated side facing downwards (**Fig. 2**). The dried, spiked blotting paper (52 mm diameter) was placed on top of the paperboard sample (B) and enclosed by the foil (C). After the equilibration period, the foil sandwich was opened and the blotting paper removed. The foil sandwich was resealed and placed onto a flat surface, with the barrier-coated side facing upwards. A die (50 mm diameter) and scalpel were used to expose the barrier-coated side of the paperboard (D). The sample was placed into the immersion cell, with the exposed barrier-coated surface facing upwards. A heaped spoonful (approximately 0.75 g) of Tenax-TA, 60/80 Mesh (Restek; Bellefonte, PA, USA) was evenly distributed across the sample surface (E). Tenax is the commercial name for modified polyethylene oxide (MPPO). It is a porous polymer that is well suited to adsorb volatiles. Its thermal stability also makes it suitable for migration testing at elevated temperatures. The immersion cell was sealed with its glass lid and placed in an oven at 60°C for 3 days (F). The migration test was performed in duplicate because of availability of sample material.

Extraction conditions

Extractions were performed using a Dionex ASE 350 accelerated solvent extractor (ASE) (Dionex; Sunnyvale, CA, USA). The ASE 350 was equipped with a solvent controller and operated at 60% rinse volume and 100 s purge. The extractions were carried out in 22 mL ASE extraction cells using acetone



2. Preparation for migration test using the immersion cell.

at 40°C. A heating time of 5 min and a static time of 10 min was used, with two cycles for each cell.

Paperboard

The paperboard was cut into small pieces approximately 1 cm × 1 cm in size. A 22 mL ASE extraction cell, with a cellulose filter fitted in the base, was filled with approximately 5 g of the paperboard sample and spiked with 25 μL of a 100 ppm d-DBP internal standard solution.

Tenax

After the migration test period, the Tenax was decanted into a 22 mL ASE extraction cell, fitted with a cellulose filter in the base, and spiked with 25μL of a 100 ppm d-DBP internal standard solution.

Recovery analysis

A heaped spoonful (approximately 0.75 g) of Tenax was placed into a 22 mL ASE extraction cell, with a cellulose filter fitted in the base. 250 μL of one of the calibration standards was added to the ASE cell and exposed to the extraction conditions as described previously. The sample extract was concentrated and quantified (C_1) by GC-MS. The same calibration standard was quantified (C_2) without being exposed to the extraction conditions. The two concentrations were used to calculate the percent recovery, as shown in Eq. (4):

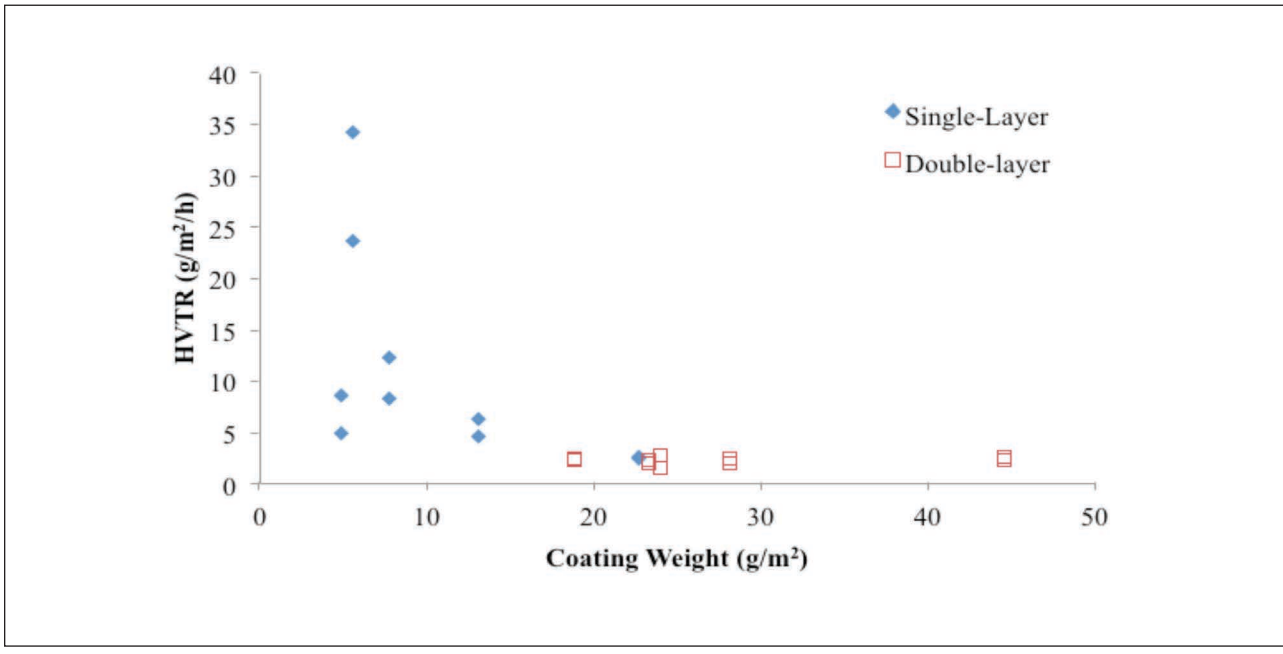
$$\%\text{Recovery} = \frac{C_1}{C_2} \times 100 \quad (4)$$

Extract concentration

A TurboVap LV concentration evaporator workstation (Biotage; Uppsala, Sweden) was used to concentrate the sample extracts. The sample extracts obtained from the Dionex ASE 350 were concentrated under a constant stream of nitrogen at 40°C until approximately 1 mL of the extract remained in the ASE vial. The concentrated extract was decanted into a 1.5 mL vial to approximately one third of the volume of the vial. The vial was then filled with acetone and the vial closed with the screw-cap lid.

GC-MS analysis

Samples were analyzed with a Thermo Scientific Trace Ultra gas chromatograph fitted with a Thermo Scientific ISQ mass selective (MS) detector (Thermo Fisher Scientific; Waltham, MA, USA). A 5% phenyl, 95% polysiloxane capillary column with a length of 30 m and an internal diameter of 0.25 mm was used. The column temperature program started at 40°C for 2 min. The temperature was ramped at 15°C/min incre-



3. HVTR as a function of coating weight for the polyvinylidene chloride (PVDC) barrier polymer, with the single-layer and double-layer coatings showing a relative standard deviation of 24% and 15%, respectively.

ments to 280°C and held constant for 15 min. Thereafter, the temperature was reduced to 200°C for 10 min as a post-run conditioning. Helium was used as the carrier gas at a constant flow rate of 1.2 mL/min with the vacuum compensation on. The injector port was maintained at 220°C and 1 μL of a sample was injected in splitless mode. The ISQ-MS was operated in electron impact ionization mode, scanning from 35 to 650 u, with a dwell time of 200 ms. The time-scheduled selected ion monitoring mode was used for quantification, using m/z 149 for the native phthalates and m/z 153 for the deuterated phthalate. The MS transfer line temperature was maintained at 280°C and the ion source at 200°C.

Limit of detection

The limit of detection was determined as the lowest concentration where the signal-to-noise ratio (*S/N*) was ≥3. The calibration standard with the lowest concentration was diluted and injected into the GC-MS. The intensity of the signal peak (i.e., DiBP, DBP, and DEHP) was determined and compared with the intensity of the baseline noise. If $S/N > 3$, the calibration standard was further diluted and the injection repeated until $S/N \leq 3$.

Limit of quantification

A quantification range was defined in this study instead of a limit of quantification. The quantification range was 2.0-1250 μg in 10 mL.

Surface defect test

Methanol was applied to the surface of coated paperboard (10 cm × 10 cm) and inspected visually for defects. Surface defects, such as cracks and pinholes, will appear as darkened areas on the surface.

Pinhole density

An image of the coated paperboard substrate was captured during the surface defect test. A grid comprised of 100 blocks was applied to the surface defect test image. The number of blocks in the grid occupied by at least one pinhole were counted and expressed as a percentage.

RESULTS AND DISCUSSION

Migration mechanism for the HVTR test

The thickness of the PVDC barrier film was varied by using coating rods with different winding thicknesses and by preparing single-layer and double-layer configurations. The film thickness was measured indirectly by determining the coating weight of the barrier film and the effect of the change in coating weight on HVTR was evaluated (**Fig. 3**). The HVTR initially declined as the coating weight increased from 5 g/m² to 20 g/m², which represented the single-layer configurations. No further reduction in HVTR was observed for coating weights exceeding 20 g/m², which represented the double-layer configurations.

Weiss [5,9] observed a similar behavior for polymer films that were coated with aluminum by vacuum vaporization and attributed the observed behavior to the presence of pinholes. This type of behavior has also been attributed to the minimum amount of coating required for complete coverage of the substrate [5].

To confirm the presence of pinholes on the PVDC barrier-coated samples, a "surface defect test" was performed.



First single-layer configuration
Coating weight = 6 g/m²



Single-layer configuration
Coating weight = 5 g/m²



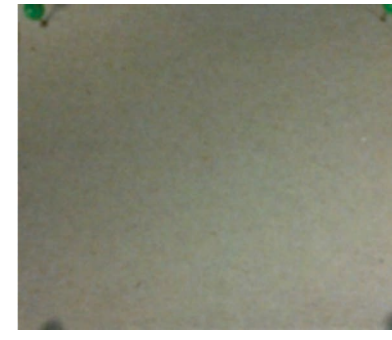
Single-layer configuration
Coating weight = 8 g/m²



Single-layer configuration
Coating weight = 13 g/m²

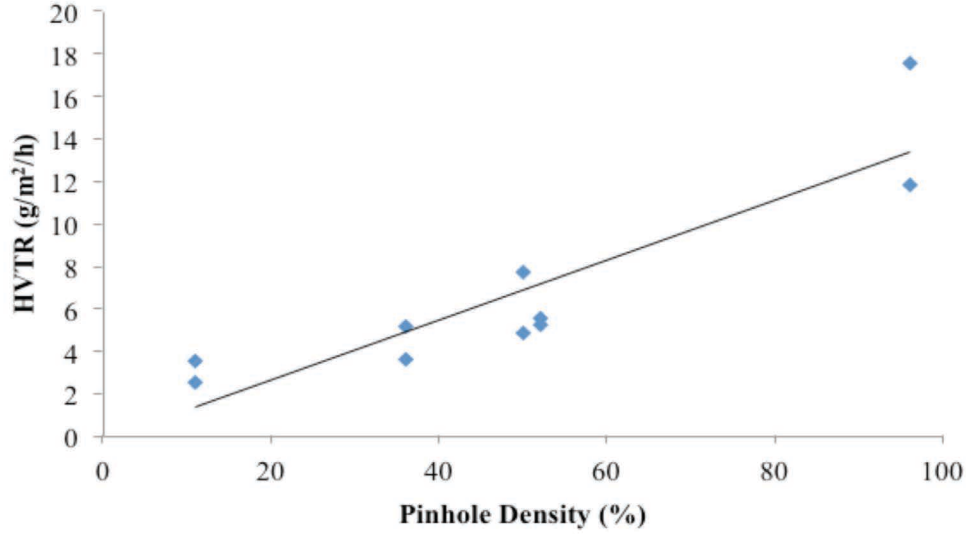


Single-layer configuration
Coating weight = 23 g/m²

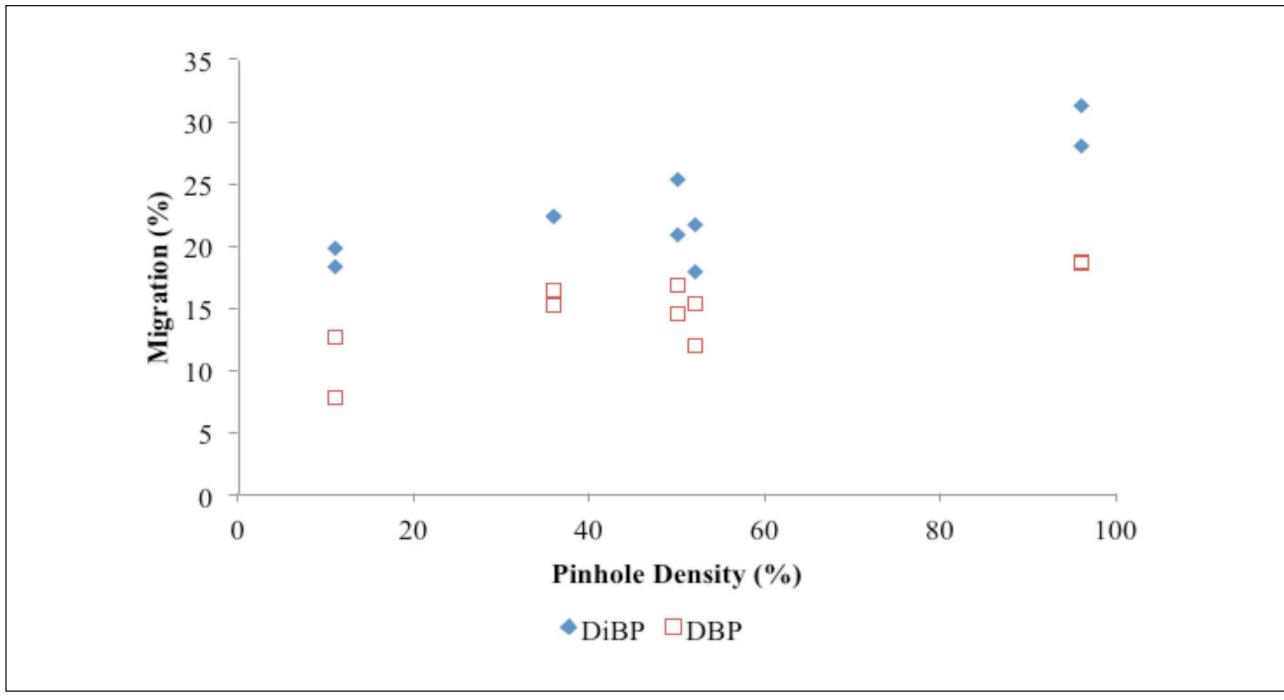


Double-layer configuration
Coating weight = 45 g/m²

4. Surface defect test. Single layer configurations and a double layer configuration are shown.



5. The effect of pinhole density on HVTR, where the coating weight is kept constant, with R = 0.9 and 22% relative standard deviation.



6. The effect of pinhole density on the specific migration of di-n-butyl phthalate (DBP) and di-iso-butyl phthalate (DiBP) where the coating weight is kept constant. DBP and DiBP showed relative standard deviation of 8% and 13%, respectively.

Methanol was applied to the surface of coated paperboard (10 cm × 10 cm) and inspected visually for defects. Surface defects, such as cracks and pinholes, appear as darkened areas on the surface. **Figure 4** shows images of the surface defect test for the single-layer configurations and one double-layer configuration. The single-layer configurations all showed numerous pinholes, with a consistent decrease in pinhole density as the coating weight increased. In the case of the double-layer configurations, no pinholes were observed.

Two mechanisms are used to describe the transport of gases and vapors through a barrier film that are either dependent on the presence of pinholes or coating weight. The data presented in Fig. 3 could indicate that the HVTR is dependent on pinhole density rather than coating weight. This is because the HVTR decreased in the case of the single-layer coatings where pinholes were observed, but remained constant in the case of the double-layer coatings where no pinholes were observed, irrespective of coating weight. However, in the case of the single-layer configurations, the pinhole density and the coating weight were varied. To confirm the transport model for HVTR, single-layer coating configurations were prepared where the coating weight was kept constant and the pinhole density was varied.

Figure 5 shows the relationship between the pinhole densities and HVTR, where the coating weight was kept constant at 29 g/m^2. The HVTR value increases linearly as a function of pinhole density. This confirmed that the transport mechanism for the HVTR test conforms to the defect model and is controlled by the presence of pinholes on the film surface.

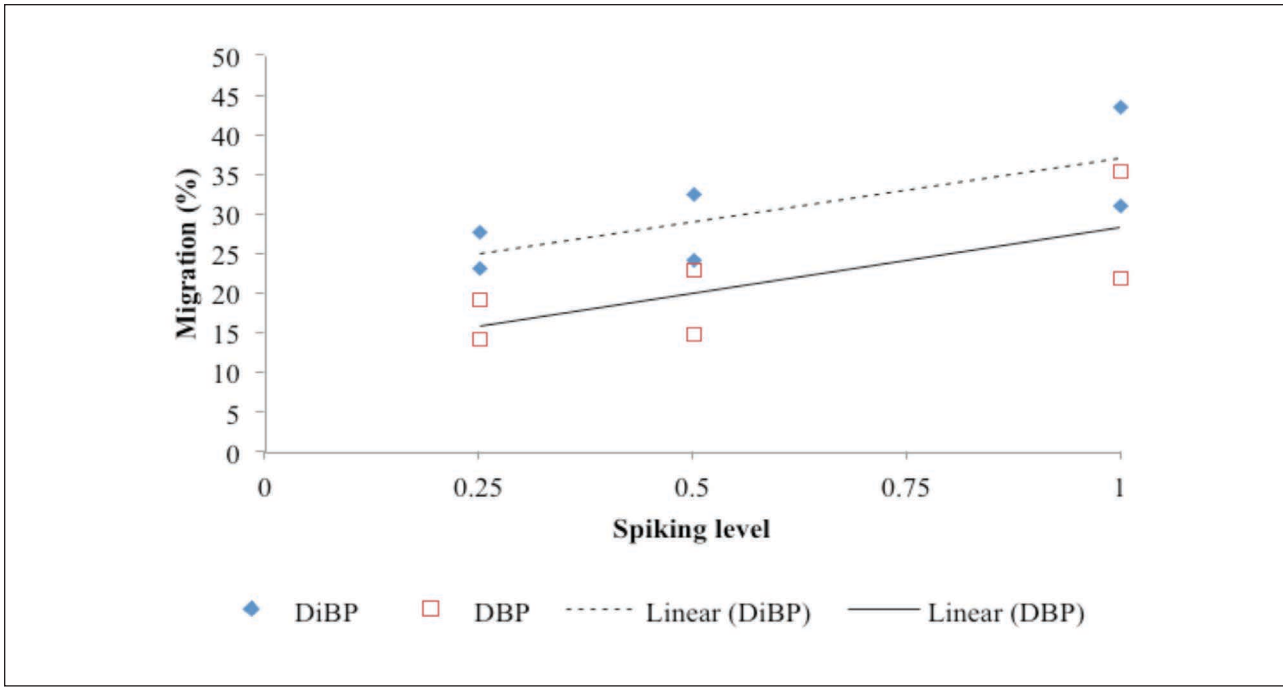
Migration mechanism for the specific migration

A limit of detection of 0.2 μg in 10 mL was found for DiBP and DBP. The recoveries for DiBP and DBP were determined to be 95% and 91%, respectively.

The same single-layer coating configurations used to determine the relationship between the pinhole density and the HVTR were also used to evaluate the relationship between pinhole density and the specific migration of DiBP and DBP (**Fig. 6**). The specific migration of DiBP and DBP were found to be similar across the low range of pinhole density up to 50%. Thereafter, only a slight increase in specific migration was observed between 50% and 95%, most likely because of the size and distribution of the pinholes on the sample surface. This shows that the defect model does not apply to the specific migration of DiBP and DBP, but is rather controlled by the diffusive-flow mechanism where the transport mechanism is dependent on the coating weight and independent of surface defects. However, properties specific to the contaminants, such as vapor pressure, also need to be considered.

Validation parameters required for implementation of a quality control level correlation

The transport mechanisms for the HVTR test and the specific migration test are different, thus making a direct correlation between the two implausible. However, an indirect correlation could be established. A general model is suggested whereby HVTR could give an indication of film integrity because the transport mechanism is dependent on pinholes. After establishing that the film integrity is sufficient, specific migration can be estimated by monitoring the coating weight be-



7. Effect of the spiking level on the specific migration of DBP and DiBP for a barrier film with a coating weight = 8.0 g/m². DiBP and DBP showed relative deviation of 19% and 28%, respectively, and each showed a correlation coefficient of R = 0.7.

cause the transport mechanism is dependent on coating weight. However, before such a model can be used, a number of variables, such as the spiking method, testing temperature, and vapor pressure of the contaminants (to name a few) require further inspection to verify its validity.

Spiking

The concentration of the chemical contaminant present in the paperboard affects the amount of migration through the barrier film [10]. The spiking level used in this study was selected to be 20 times the legal migration limit to ensure that measureable migration was observed. However, in commercial applications, the levels of these chemical contaminants present in the paperboard should be significantly lower than the legal migration limits.

To evaluate the effect of DiBP and DBP concentrations present in the paperboard on the amount of migration through the PVDC film, the spiking concentration was reduced to 50% and 25% of the original spiking level and the migration test was performed at 60°C for 3 days. **Figure 7** shows the change in the percentage specific migration of DiBP and DBP as a function of spiking level for the PVDC film with a coating weight of 8.0 g/m². The percentage specific migration of DiBP and DBP decreases as the spiking level is decreased and a linear correlation is observed. However, when the linear trend line is extrapolated to zero, it grossly over-estimates the migration of DiBP and DBP at zero concentration. This could indicate that there is a spiking level limit, above which it can no longer be used to predict migration levels from commercial use paperboard samples. Further work will be required to determine the spiking levels that better estimate migration levels.

Another possible explanation for the over-estimation of DiBP and DBP migration could be related to the spiking method used. Even though the spiked blotting paper was placed in contact with the non-coated side of the paperboard samples, spiking was done in an enclosed system. As such, DiBP and DBP could have partitioned into the vapor phase and saturated the coated side of the paperboard. Thus, the measured migration would indicate the chemical contaminants present on the coated surface rather than the transport of the chemical contaminants from the bulk of the paperboard through the barrier film. This could provide an explanation for the over-estimation of migration observed previously. Optimization of the spiking method would be necessary to ensure that the coated surface is not contaminated during spiking.

Temperature

Care must be taken when using elevated temperatures for migration testing of barrier-coated paperboard. The glass transition temperature (Tg) of the binder system of the coating is an important parameter to consider. During the preparatory stages of this study, a number of different barrier polymers were evaluated that had different chemical structures, barrier efficiency, and glass transition temperatures. In particular, one of the barrier polymers had a Tg = 40°C. If this particular barrier polymer were to be used in breakfast cereal packaging that is stored at ambient temperature (23°C), the polymer would be in the glassy state (T < Tg). However,

at the accelerated conditions used in this study (i.e., 60ºC), the polymer would be in the rubbery state (T > Tg).

The transport behavior of a contaminant through a barrier film is noticeably different above and below the glass transition temperature [11]. Below the glass transition temperature, contaminant transport generally follows a dual-mode sorption model, whereas above the glass transition temperature, a single-mode diffusion model generally applies [11-13]. It is therefore essential that the polymer be in the same state at the actual conditions of use and at the elevated temperatures used in accelerated testing to ensure that the migration mechanisms are comparable.

Fortunately, the PVDC barrier used in this study has a Tg = 16.6°C, and as such, will be in the rubbery state at 60°C (the accelerated testing temperature) and at ambient temperature should the PVDC barrier be used for breakfast cereal packaging stored at 23ºC. However, the permeability of a polymer film is increased by temperature, the extent of which varies for different polymers [10,13]. Increased temperature also increases the partition coefficient of the contaminant, which will result in increased migration [14]. This might give a false indication of migration potential of contaminants from paperboard packaging used at ambient temperatures in actual use.

Model Contaminant	Vapor Pressure at 20ºC-25ºC, kPa
DiBP	1.0 x 10-5
DBP	9.7 x 10-6
DEHP	1.3 x 10-8

I. Vapor pressure of model contaminants.

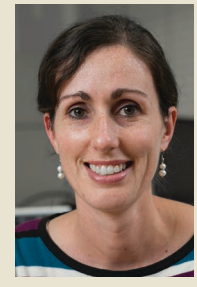
Contaminant vapor pressure

DEHP was initially included as one of the model contaminants in this study. However, negligible migration was observed in comparison with the levels observed for DiBP and DBP. This is most likely related to the difference in vapor pressure between the three phthalates (**Table I**) [15]. DEHP has the low-

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The food packaging industry has been prompted to investigate the feasibility of using paperboard packaging materials manufactured from recycled fiber. Testing the compliance of these paperboard products to international food safety standards is very costly and requires a high level of operator expertise. A simplified permeation method that simulates the migration of organic vapors can be used on a production level to monitor the barrier efficiencies of coated paperboard products. However, as yet, no correlation exists between the actual migration and the simplified permeation method. Such a correlation would allow paperboard manufacturers to estimate the barrier efficiency of coated paperboard products to specific contaminants on a production level.

Previous research aimed at evaluating the barrier properties of coated paperboard products has either been solely focused on actual migration methods or the permeation method. However, to date, there is no record of a correlation being established between the two methods as outlined in this study.

The migration of chemical contaminants through barrier-coated paperboard is affected by a vast number of variables related to environmental conditions, nature of the contaminant, and paperboard properties. Where possible, migration experiments were conducted by only changing one variable at a time to evaluate the effect on migration.

The most surprising part of this work was the difference in the migration mechanisms associated with the permeation method and the actual migration.

A correlation of this nature will allow paperboard manufacturers to estimate the barrier property efficiency of coated paperboard to organic vapors on a quality control level. This will allow paperboard manufacturers to predict the barrier property of coated paperboard to specific chemical contaminants such as DiBP and DBP.

The accelerated tested conditions used in this study will need to be validated to confirm that they correlate with actual conditions of use.

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est vapor pressure, and as such, will partition into the vapor phase at a much slower rate than DiBP and DBP. This observation highlights that apart from the migration mechanism being dependent on the presence of the pinholes, properties specific to the contaminant, such as vapor pressure, also influence the tendency for migration through barrier films.

CONCLUSION

The transport of volatile organic vapors and gases through thin barrier films can occur via two mechanisms. In the case of the HVTR test, the defect model applies; in the case of specific migration, the diffusive flow model applies. Therefore, a direct correlation between HVTR and specific migration could not be established. However, it appears that an indirect correlation is possible. The HVTR can be monitored on a production-scale as an indicator of film integrity. After determining that the HVTR falls below a specific value, the coating weight of the coated paperboard product can be used to estimate the expected barrier property. The accelerated testing conditions used in this study will need to be validated to confirm that they correlate with actual conditions of use before such a correlation tool can be implemented on production scale. **TJ**

ACKNOWLEDGEMENTS

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LITERATURE CITED

1. Diesen, M., *Economics of the Pulp and Paper Industry*, 2nd edn., Finnish Paper Engineers' Association, Helsinki, 2007, Chap. 1.
2. Escabasse, J.Y. and Ottenio, D., *Food Addit. Contam.* 19(Suppl): 79(2002).
3. U.S. Food and Drug Administration, *21 CFR 176.260 - Pulp from reclaimed fiber*, U.S. Food and Drug Administration, Silver Spring, MD, USA, 2014. Available [Online] http://www.accessdata.fda.gov/scripts/cdrh/cfdocs/cfcfr/CFRSearch.cfm?fr=176.260 <16April2015>.
4. Triantafyllou, V.I., Akrida-Demertzi, K., and Demertzis, P.G., *Food Chem.* 101(4): 1759(2007).
5. Chatham, H., *Surf. Coat. Technol.* 78(1-3): 1(1996).
6. Prins, W. and Hermans, J.J., *J. Phys. Chem.* 63(5): 716(1959).
7. Tiggelman, I., Pasch, H., and Hartmann, P.C., *TAPPI J.* 11(6): 41(2012).
8. Poças, M.F., Oliveira, J.C., Pereira, J.R., et al., *Food Control* 22(2): 303(2001).
9. Weiss, J. and Leppin, C.H., *Thin Solid Films* 174(1): 155(1989).
10. Rogers, C.E., in *Polymer Permeability* (J. Comyn, Ed.), Chapman & Hall, London, England, 1985, Chap. 2.
11. Klopffer, M.H. and Flaconneche, B., *Oil Gas Sci. Technol.* 56(3): 223(2001).
12. Stern, S.A. and Trohalaki, S., in *Barrier Polymers and Structures* (W.J. Koros, Ed.), American Chemical Society, Washington, DC, 1990, Chap. 2.
13. Weinkauf, D.H. and Paul, D.R., in *Barrier Polymers and Structures* (W.J. Koros, Ed.), American Chemical Society, Washington, DC, 1990, Chap. 3.
14. Triantafyllou, V.I., Akrida-Demertzi, K., and Demertzis, P.G., *J. Chromatogr. A* 1077(1): 74(2005).
15. Australian Government Department of Health, National Industrial Chemicals Notification and Assessment Scheme (NICNAS), *Phthalates hazard assessment reports*, Australian Government Department of Health, Sydney, Australia, 2007. Available [Online] http://www.nicnas.gov.au/chemical-information/other-assessment-reports/phthalates-hazard-assessment-reports <14April2015>.