Relationship between Mass Transfer of Permeants and Polymer Processing

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Abstract
Assessing the mass transfer of permeants through a polymer material is of key importance when determining the material’s end use. Mass transfer of permeants through polymer membranes strongly depends on polymer morphology. Since polymer processing impacts the polymer morphology, our objective is to evaluate the relationship between mass transfer of permeants and polymer processing. A gravimetric system, including a Rubotherm electrobalance, was used to demonstrate important differences in the solubility parameters of benzaldehyde on polypropylene resin, sheet, and a thermoformed polyhedron container.

Introduction
With the increasing use of polymers as food and pharmaceutical packaging materials, more attention has been paid to the moisture, gas, and organic barrier properties of polymeric packaging materials [1]. The sorption of organic compounds from food and pharmaceutical products into polymers (i.e., scalping) is a factor in product quality alteration during storage. Scalping can reduce the flavor intensity or can change the flavor profile of the packaged product. Furthermore, sorption of organic components can affect the package integrity or damage the package material by causing delamination or polymer swelling, thus leading to further sorption and eventually reducing the shelf-life of the packaged product. Therefore, the study of mass transfer has practical significance, especially the sorption of organic compounds through polymer structures [2].

Several methods have been used for measuring the mass transfer characteristics of polymer films or sheets, including an isostatic permeation procedure [3, 4], a quasi-isostatic permeability method [3, 5], a thermal stripping/thermal desorption (TS/TD) procedure [6], and gravimetric techniques [7, 8]. The study of mass transfer in a container system by using a sorption cell has been reported, where the permeant was dissolved or suspended in a liquid and brought into contact with the polymer [9]. In that case, components such as aqueous media or solvents used to disperse organic compounds may have affected the partitioning. Gravimetric analysis is very suitable for the determination of the solubility coefficient (S). The advantages of gravimetric analysis include the simplicity in the sample manipulation and also in the continuous recording of weight gain by the test specimen as a function of time. Gravimetric analysis permits accurate and direct measurement of the sorbate uptake at both transient and steady state ($M_\infty$). The $M_\infty$ value obtained at steady state can be used to calculate $S$ [6, 7].

Many of the current permeability data of organic compounds have only been obtained for flat films or sheets, and these values are then used to calculate the barrier properties of containers [10, 11]. In general, the polymer forming processes by which containers are produced, such as blow molding, injection blow molding, and thermoforming, cause changes within the polymer structure and morphology. The processing induces localized effects and stresses in the final container that may produce variations in the barrier properties of the formed container compared with the film or sheet [12]. The differences in the barrier properties between container and unformed polymer sheets may be substantial. Using the permeability data generated from films and sheets to calculate container permeability will thus cause some error in the prediction of the container barrier properties.

The objectives of this work include: (1) to develop a methodology to evaluate the sorption of organic and moisture vapors by a gravimetric method using a Rubotherm microbalance; (2) to compare the sorption of organic vapors in polymer resin, sheet, and containers; (3) to demonstrate the impact of polymer processing on the sorption of organic compounds by the polymer; and (4) to study the sorption of organic and moisture vapors on a polymer simultaneously.

Experimental
Materials

Benzaldehyde (BA), purified by redistillation, ≥ 99.5% purity, with a density of 1.045 g/cm$^3$, was obtained from Aldrich Chemical Company. BA was used as the sorbate/permeant in this study. BA has been well identified as a natural flavor compound and is the characteristic impact flavor of cherries and almonds.

Polypropylene (PP) resin, with a density of 0.900 g/cm$^3$ and melt flow index between 2.5-3.1 g/10 min, was obtained from ExxonMobil Chemical Company (Baytown, TX). PP is not a very good organic barrier, but it is useful for demonstrating the impact of polymer processing on the sorption of organic compounds under selected conditions.

Atactic polypropylene (PP), a totally amorphous waxy solid with specific gravity 0.85 g/cm$^3$ and $M_w$ of 12,000 g/mol, was obtained from Scientific Polymer products, Inc (Ontario, NY) and was consider as a reference material.
Instrument

Sorption studies using the continuous flow method [8,13] were conducted on a Rubotherm SGA-100R gravimetric analyzer obtained from VTI Corporation (Hialeah, FL). This instrument has been specially designed to provide thermal stability and maximize performance. The magnetic suspension balance has 10 g capacity, 1 μg resolution, and a chamber big enough to hold a container. The balance comes with a dew point analyzer (DPA) for controlling the relative humidity (RH). It also has three vapor generators/mass flow controllers to generate, within the chamber, different vapor concentrations of one organic compound or a combination of organic compounds and moisture. Figure 1 shows the schematic of the gas flow of the gravimetric equipment.

Experimental Procedure

Samples of PP were placed in the sample basket and suspended within the chamber. A specific concentration of BA vapor was generated by mixing dry nitrogen through the wet and dry mass flow controllers. The mixture was introduced to the sample chamber through the appropriate valve. The organic vapor concentration was controlled by adjusting the ingredients of mixed flow gases. The sorption results were adjusted to compensate for the drifting effect of the balance by calibrating the balance before each sorption test and by correcting the zero every 10 minutes throughout the measurements. This was done in order to correct for buoyancy on the suspension magnet and any inner parts of the magnetic coupling that were lifted together with the sample. The weight gain of the polymer sample in sorption was continuously monitored and recorded at 25°C. Experiments were continued until the sorption equilibrium criterion had been reached.

Results and Discussion

Polymeric container manufacturing

Polypropylene resin pellets were considered as the starting material in this study. PP sheets with a thickness of 0.51 mm (20 mil) were then formed by extrusion and casting from PP resin by a Killion KLB100 extruder (Cedar Grove, NJ). A polyhedron container, was designed (figure 2). The containers were thermoformed on a Hydro-Trim 1620 thermoformer (West Nyak, NY) through male molds. The polyhedron container represented those containers that have several corners and edges.

Benzaldehyde Uptake in Different PP shapes

A method was developed to study the sorption of benzaldehyde and moisture vapors by a continuous gravimetric method via a Rubotherm SGA-100R magnetic suspension microbalance. The sorption of benzaldehyde by PP resin, sheet, and containers was studied by continuously recording the weight gain of the polymer when exposed to specific concentrations of benzaldehyde. Five organic vapor activities (VA) were chosen: 0.1, 0.3, 0.5, 0.7, and 0.9. The balance equilibrium criterion was a 0.0001 % weight change in 20 mins or 10,000 minutes.

Figure 3 shows the sorption of benzaldehyde by PP resin, sheet, thermoformed sheet and atatic PP studied by continuously recording the weight gain of polymer when exposed to benzaldehyde vapor at vapor activity of 0.3 at 25 ºC. Based on the sorption curves in Figure 3 the thermoformed sheet gained more weight (0.489 %) than PP sheet (0.271 %) and resin (0.077 %) at same vapor pressure.

Normally when polymer is processed, the internal stresses will be set up and the heat treatment during the processing imparts the molecular chains energy and mobility to rearrange themselves towards the conformational changes. The polymer morphology, including crystallinity, crystal size, the distance between the lamellas, free volume and surface contour will all be changed according to the processing conditions. As mentioned before that sorption behavior of polymer is closely related to the polymer morphology, thus the polymer processing, which causes morphology changes, should cause different sorption behavior for different thermoprocessed polymers. The processing effect on sorption is clearly demonstrated in Figure 3. Furthermore, the sorption of benzaldehyde in atatic PP was used as a reference to compare with that in other PP forms (resin, sheet and thermoformed sheet). The high sorption ability of atatic PP (0.989 %) supports the morphology effect in the organic sorption in polymer.

Impact of Vapor Activity of Benzaldehyde on the Sorption Behavior

The processing effect on the sorption of benzaldehyde in PP has been demonstrated in Fig.3 at vapor activity of 0.3. The similar processing effect was also observed in vapor activity of 0.5 and 0.9. The comparison is shown in Figure 4. It is found...
that for each PP form (resin, sheet, thermoformed sheet or atatic PP), the sorption capability increases as the organic vapor pressure increases. Besides, the higher the VA, the larger the sorption difference was observed among the different PP forms.

Summary

A gravimetric method was developed to evaluate the sorption of benzaldehyde and moisture vapors by PP via a Rubotherm microbalance. Sorption results were compared among three PP forms (resin, sheet, and containers. The results clearly demonstrated that the sorption of BA was affected by different PP forms and also by container shapes. These results were consistent with our expectation that the forming process of a polymer induces localized effects and stresses that cause changes in polymer structure and morphology, thus affecting barrier properties and sorption of organic vapors.

Acknowledgments

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References


Keywords

Sorption, barrier, benzaldehyde, polypropylene, container, gravimetric, microbalance.
Figure 1. Schematic of gas flow in Rubotherm SGA-100R gravimetric analyzer

Figure 2. Thermoformed polyhedron shape
Figure 3. Sorption curves for benzaldehyde vapor in PP with vapor activity of 0.3 at 25 °C. From bottom to top: sorption in a) resin pellets, b) sheet, c) thermoformed sheet and d) atatic PP.

Figure 4. Sorption curves for benzaldehyde vapor in PP at 25 °C at vapor activity of 0.5 (left) and 0.9 (right). From bottom to top: PP resin, sheet, thermoformed sheet and atatic PP.
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Outline

- Background
- Motivation
- Objectives
- Research Work
- Conclusion
- Recommendations
Background

- Increasing use of plastics as food / pharmaceutical packaging material

- Barrier properties of polymer ↔ Mass transfer
  - Sorption
  - Migration
  - Desorption

- Permeants: Organic compounds, moisture

- Combination of permeants
Impact of Mass Transfer on:

- On product
- On package
Factors affecting the mass transfer cont..

- Environmental conditions: T, RH
- Chemical structure of the polymer chain
- Affinity of sorbate to polymer
- Polymer morphology
  - crystallinity, free volume, surface property, surface to bulk ratio, vapor activity
- Processing history
Motivation

1. Mass transfer assessment has mainly been done on sheets
   What about container?

2. Polymer processing has effect on the mass transfer properties of polymer
   How does the processing change the sorption and diffusion?

3. It is possible to access the polymer morphology characteristics through sorption and diffusion
Methods to measure the permeation of organic compounds in polymer:

1. polymer films / sheets:
   - isostatic procedure
   - quasi-isostatic method
   - thermal stripping / thermal desorption (TS/TD)
   - **Gravimetric technique**

2. container system:
   - sorption cell method
Gravimetric technique

- Monitor permeant uptake
  - Solubility coefficient
  - Diffusion coefficient
Solubility Coefficient ($S$)

- $S$ is an equilibrium partition coefficient for distribution of the penetrant between polymer and vapor phase.

\[
S = \frac{C_p}{C_v} = \frac{M_\infty}{\nu \cdot P}
\]

- Gravimetric method:
  
  $S = \text{weight gain [g/g]} \times \text{polymer density} / \text{vapor pressure}$
Diffusion Coefficient ($D$)

Polymer Film/sheet

\[
\frac{M_t}{M_\infty} = 1 - \frac{8}{\pi^2} \left[ \exp\left(\frac{-D\pi^2 t}{l^2}\right) + \frac{1}{9} \exp\left(\frac{-9D\pi^2 t}{l^2}\right) \right]
\]

\[
D_s = \frac{0.049l^2}{t_{0.5}}
\]

The value of $t_{0.5}$ can be obtained graphically.
Objectives

- To compare the sorption of organic vapor in rubbery polymeric resin, sheet and container

- To demonstrate the effect of manufacturing on sorption of organics

- The implementation of the new SGA-100R gravimetric analyzer
Research Work: Materials & Methods

- **Organic sorbate:**
  - Benzaldehyde (BA), 99.5+%
    - Five vapor activities: 0.1, 0.3, 0.5, 0.7 and 0.9

- **Polymer:**
  - Polypropylene (PP) resin:
    - Mt: 250,000 g/mol, Mt/Mn = 4.2
    - Crystallinity = 39.4%, Density = 0.9 g/cm³
  - Atactic PP:
    - Crystallinity = 0 %, Density = 0.85 g/cm³
Polymer Processing

- Casting PP Sheet
  thickness of ~ 18 mil (~0.46 mm),
  width of 6 in (~15 cm)

- Thermoforming PP container
  by male mode
  surface area of 36.3 cm\(^2\)
SGA-100R gravimetric analyzer including Rubotherm magnetic suspension microbalance (VTI corp. Hialeah, FL)
Figure 3. Coupling/decoupling action between the electromagnet and suspension magnet under different operation condition.
Results and Discussion

- Sorption kinetics
- Effect of surface and bulk on sorption
- Comparison of benzaldehyde uptake in PP resin, sheet and container: effect of polymer processing
- Sorption kinetics: measurements
Results and Discussion cont..

Sorption kinetics:

- Sorption in resin at high vapor activities: two-stage
- Sorption in resin at low vapor activities: one-stage
- Sorption in Sheet and container: one-stage
Sorption of BA in resin at high vapor activity (0.7): two-stage sorption
Sorption of BA in PP resin at 25 °C

![Graph showing wt. change vs. time for different VA values.](image-url)
Kinetic sorption

- Sorption in resin at high vapor activities: two-stage
- Sorption in resin at low vapor activities: one-stage
- Sorption in Sheet and container: one-stage
Sorption of BA vapor in PP sheet (L)/container (R)

PP Sheet

- VA0.9
- VA0.7
- VA0.5
- VA0.3
- VA0.1

PP Polyhedron container

- VA0.9
- VA0.7
- VA0.5
- VA0.3
- VA0.1
Results and Discussion

- Kinetic sorption

- Effect of surface and bulk characteristics on sorption

- Comparison of benzaldehyde uptake in PP resin, sheet and container: effect of polymer processing

- Sorption kinetics measurements
Sorption curves for BA vapor in PP at vapor activity of 0.5 at 25 °C
Results cont...

- Kinetic sorption

- Effect of surface and bulk characteristics on sorption

- Comparison of BA uptake in PP resin, sheet and container: effect of polymer processing

- Sorption kinetics measurements
Sorption curves for BA in PP at vapor activity of 0.3 (L) and 0.9 (R)
Results cont...

- Kinetic sorption

- Effect of surface and bulk characteristics on sorption

- Comparison of benzaldehyde uptake in PP resin, sheet and container: effect of polymer processing

- Sorption kinetics measurements
### Percent Wt. Gain of BA-PP at 25 °C

<table>
<thead>
<tr>
<th>Vapor activity [pa/pa]</th>
<th>Resin % Wt. Gain [% ( g_B / g_{PP} )]</th>
<th>Sheet % Wt. Gain [% ( g_B / g_{PP} )]</th>
<th>Polyhedron container % Wt. Gain [% ( g_B / g_{PP} )]</th>
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<tbody>
<tr>
<td>0.1</td>
<td>---</td>
<td>0.053</td>
<td>0.189</td>
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<tr>
<td>0.3</td>
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<td>0.275</td>
<td>1.087</td>
<td>1.140</td>
</tr>
<tr>
<td>0.9</td>
<td>0.440</td>
<td>1.735</td>
<td>3.135</td>
</tr>
</tbody>
</table>
Conclusion

- A gravimetric method was developed to evaluate the sorption of organic vapor by polymer resin, sheet and container via a SGA100R gravimetric system.

- The converting process impact the sorption of BA on PP.
Conclusion cont....

- Two-stage sorption was observed in PP resin at high vapor activities

- It was found that the following factors impact sorption:
  - surface characteristics
  - polymer bulk properties
  - geometry
  - morphology
Recommendations

- To determine how the polymer bulk property and surface property affect the sorption process, and how does each factor contribute to the sorption properties.

- To compare solubility coefficient and diffusion coefficients in different PP forms.
Recommendations cont...

- To develop tools that allow us to assess morphology as sorption or de-sorption is taking place

- To predict polymer characteristics through sorption assessment
Thank You

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