Impact of Polymer Processing on Sorption of Benzaldehyde Vapor in Amorphous and Semicrystalline Polypropylene

Ying Qin,[1] Maria Rubino,[2] Rafael Auras,[2] Loong-Tak Lim[3]

[1]Center for Green Manufacturing, University of Alabama, Tuscaloosa, Alabama
[2]School of Packaging, Michigan State University, East Lansing, Michigan
[3]Department of Food Science, University of Guelph, Guelph, Ontario, Canada

ABSTRACT: In this study, organic vapor sorption properties of different polypropylene (PP) forms (resin, sheet, thermoformed sheet, and atactic PP) at 25°C were investigated. The sorption of benzaldehyde at five vapor activities was studied by using a continuous gravimetric method. The sorption of benzaldehyde vapor in PP exhibited different behaviors among resin, sheet, and polyhedron thermoformed sheet. The experimental results demonstrated that the extrusion and thermoforming processes used for forming these parts had a great impact on the sorption behavior because of the changes in surface and bulk morphologies, especially at high vapor activities. © 2008 Wiley Periodicals, Inc. J Appl Polym Sci 110: 1509–1514, 2008

Key words: sorption; polypropylene; gravimetric method; processing; morphology

INTRODUCTION

The use of thermoplastic polymers in food and pharmaceutical packaging materials has increased rapidly and continued to grow in the recent years. Along with the increased use of new high barrier polymers in packaging applications, there is a need to assess the mass transfer of organic compounds for these materials.

The mass transfer process in pharmaceutical and food packaging can be described as a multistep event, which is characterized by the collision and sorption of permeant molecules on the surface of polymer, diffusion through the polymer matrix, and desorption of the permeant from the low concentration surface of the polymer.[1] Mass transfer properties of polymers, especially sorption and diffusion properties, are determined by polymer chemical structure, morphology, and surface characteristics. For a given sorbant-polymer system subjected to specific conditions, the sorption process is mainly controlled by the polymer morphology, such as crystallinity and free volume.[2]

Morphology plays a major role in the mass transfer process. It is generally accepted that sorption and diffusion take place exclusively in the amorphous regions.[2,3] The crystalline zones can be considered as the excluded volumes for sorption and are impermeable to the permeant. More specifically, Klopffer[1] indicated that these crystalline zones have two effects on gas diffusion: (1) they increase the effective path length of diffusion and (2) they reduce the polymer chain mobility in the amorphous phase because the chain ends are trapped in the neighboring crystalline lamellae, which leads to a higher activation energy for diffusion. Michaels et al.[2,3] introduced a "tortuosity factor" and a "chain immobilization factor" to account for these effects.

In the case of amorphous or semicrystalline polymers, the solubility and diffusion coefficients S and D can be related to the free volume (V_f), which is defined as a space that is not occupied by the macromolecules.[4] According to the free volume theory put forward by Fujita,[5] it is possible to explain the dependence of D with parameters such as concentration, the penetrant shape and size, temperature, and the glass transition temperature of the polymer. Furthermore, the presence of crystalline regions may decrease the sorption of permeant within the amorphous region. The crystalline structure can also interact with the permeant, causing sorption to take place, which further influences the sorption within the amorphous region.[2]

In general, the forming processes for a polymer, such as extrusion, blow molding, injection blow molding, and thermoforming, are capable of changing the polymer morphology by redistributing the crystalline and amorphous regions and changing the available free volume. The conversion of polymer

into films, sheets, and containers is typically carried out at elevated temperature to produce a homogeneous melt (e.g., extrusion of resin) or s reheating the polymer to a process temperature so that it is soft enough for shaping (e.g., blow molding of preform). To solidify the polymer after forming, it is subjected to rapid cooling by conductive and convective heat transfer. During this quenching step, many polymers undergo glass transition, which causes their molecular chains to ''freeze'' in the direction of deformation. The molecular orientation induced may not be uniform, causing anisotropy of barrier properties for the final articles.[6] Because of the difficulties associated with the testing of the mass transfer of organics in three-dimensional thermoplastic articles, much of the current permeability data for organic compounds is derived from flat film or sheet specimens, which is then extrapolated to describe the barrier properties of three-dimensional articles.[7–9] This approach can result in large errors because of the oversimplification of the anisotropic properties of these articles.

During vapor sorption, semicrystalline polymers tend to undergo complex changes. Besides gaining in mass, structural changes within the polymer may also occur, such as relaxation of polymer chains, modification of free volume, lowering of glass transition temperature, and manifestation of a viscoelastic behavior.[10] Because of their strong interaction with compatible organic compounds, the sorption behavior of semicrystalline polymers tends to be both concentration- and time-dependent. Furthermore, the structural anisotropy that resulted from the conversion process can also affect the sorption behavior of these polymers. Although the sorption of gases and vapors has been extensively studied for polypropylene (PP),[11–13] there appear to be no published data on comparing the sorption of benzaldehyde vapor in extruded PP sheets and thermoformed article, especially on correlating the effect of polymer processing and the sorption behavior. The objectives of this study were (1) to study the benzaldehyde sorption behavior of PP as resin pellets, extruded sheets, and as a thermoformed polyhedron-shaped container; and (2) to demonstrate how changes in polymer bulk and surface morphologies affect the sorption characteristics of benzaldehyde.

EXPERIMENTAL

Materials

Benzaldehyde, purified by redistillation to ≥99.5% (Sigma-Aldrich, St. Louis, MO) was used as the sorbant, and two grades of PP were used in this study. The atactic polypropylene (PP) had a specific gravity of 0.85 g/cm³, and molecular weight (M_w) of 12,000 g/ mol (Scientific Polymer Products, Ontario, NY) and a

TABLE I
Conditions Used to Extrude the PP Sheet

Extruder parameters	Condition
Temp of zone 1 to zone 3	249°F
Temp of zone 4 (die)	283°F
Melt temp	252°F
Motor speed	112 RPM
Chill roller temp	100°F
Chill roller speed	0.86 RPM
Die gap	1.79 mm (70 mil)

paste appearence. The semicrystalline PP resin, supplied by ExxonMobil Chemical (Baytown, TX, USA), was a homopolymer produced using a Ziegler-Natta type catalyst, with M_w of 250,000 g/mol (M_w/M_n = 4.2), density of 0.90 g/cm³, melt flow rate between 2.5 to 3.1 mg/10 min, and total amount of additives of less than 0.3 wt %. The degree of crystallinity for the resin, as determined by differential scanning calorimetry (DSC), was 39.4%.

PP sheet and container processing

PP resin was extruded and cast (Table I) into PP sheets to a thickness of 0.46-mm (18 mg) and width of 15 cm (~ 6 in) using a Killion KLB100 extruder (Killion Extruder, Cedar Grove, NJ).

A polyhedron-shaped container with a surface area of 36.3 cm² was designed to represent typical packaging containers that have several corners and edges (Fig. 1). The containers were thermoformed from the PP sheet by using a Hydro-Trim 1620 thermoformer (Hydro-Trim Corp., West Nyack, NY) through a male mold; the top and bottom mold temperature controller were set at 210°C, the heating time was 40 s, and the forming time was 25 s. A male mold was chosen since it can produce containers with smaller thickness variance than the female mold.

Gravimetric method for measuring benzaldehyde sorption

A gravimetric method was used to study the sorption and diffusion behaviors of benzaldehyde in PP because of this method flexibility in accommodating different sample sizes, and ability to continuously and accurately record weight gain as a function of time during transient and steady state sorption. The sorption studies were conducted in the continuous flow mode[14,15] using a SGA-100R gravimetric analyzer (VTI, Hialeah, FL). The core portion of this system is a Rubotherm electromagnetic suspension microbalance,[16,17] which measures the weight change of the sample and allows a continuous recording of data. This microbalance possesses a sensitivity of 10.0 μg and has a contact-free magnetic suspension
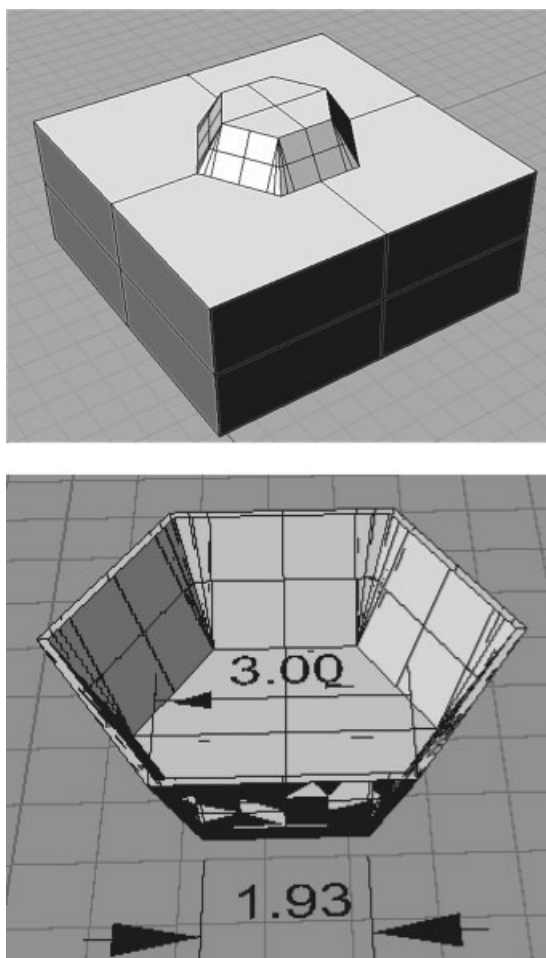
Figure 1 Schematic designs of the polyhedron-shaped male mold (left) and corresponding thermoformed container (right) in cm.

coupling which keeps the atmosphere surrounding the sample separated from the microbalance. The SGA-100R unit has a chamber size of 7.5 cm × 7.5 cm × 14 cm (L × W × H), which is large enough to hold a thermoformed polyhedron container sample. The target vapor activity and relative humidity (RH) conditions were generated and constantly maintained by a vaporizer and humidifier, respectively.

The gravimetric analyzer was designed to have a long-term stability because of the separation of its measuring cell and weighing system. The automatic decoupling of the measuring load and re-zeroing throughout the testing process enhanced the measuring accuracy, particularly during extended measurements. The balance was calibrated before each experiment and during the sorption process, and balance drift was corrected every 10 min. These procedures corrected the buoyancy of the suspension magnet and any inner parts of the magnetic coupling that were lifted together with the sample. A further description of the electrobalance, including instrument details, instrument noise and drift analy-

sis under different conditions are reported elsewhere.[17]

Benzaldehyde sorption experiments

Sorption of benzaldehyde vapor in PP was evaluated for a relatively small amount (0.15 g) a large amount (2.0 g) of resin pellets, by resin slices (eight slices cut from one resin pellet using a microtome), and atactic PP (totally amorphous) in a paste form. The resin pellets came from the same batch and had an average diameter of 0.4 cm. Prior to the sorption tests, each polymer sample was dried in a vacuum oven at 40°C for 10 h and then purged with nitrogen gas for 2 h in the balance chamber. The sorption tests were conducted at five benzaldehyde vapor activities (0.1, 0.3, 0.5, 0.7, and 0.9). The weight gain of the polymer sample during sorption was continuously monitored and recorded at 25°C and 0% RH. Equilibrium was considered achieved when the weight change was below 0.0001% in 20 min. Experiments were stopped either when the sorption equilibrium was reached or 10,000 min ($\sim$ 1 week) had passed.

RESULTS AND DISCUSSION

Effects of polymer morphology on benzaldehyde sorption in by PP

The sorption curves for PP pellets of different total starting weights were similar with equilibrium weight changes of 0.130 and 0.131% for 0.15 and 2.0 g, respectively (Fig. 2). Thus, sorption of benzaldehyde did not appear to depend on the polymer dry weight or exposed surface area. The sorption in PP resin slices (0.15 g) resulted in a weight change of 0.50% at steady state, which was considerably much higher than the sorption by the whole resin pellets (curve a). The results from the sorption of
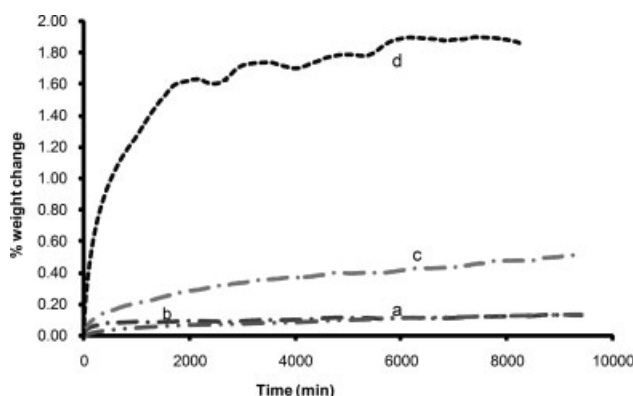
Figure 2 Sorption curves for benzaldehyde vapor in PP at vapor activity of 0.5 at 25°C. From bottom to top: (a) resin pellets (0.15 g), (b) resin pellets (2.0 g), (c) resin slices, and (d) atactic PP.
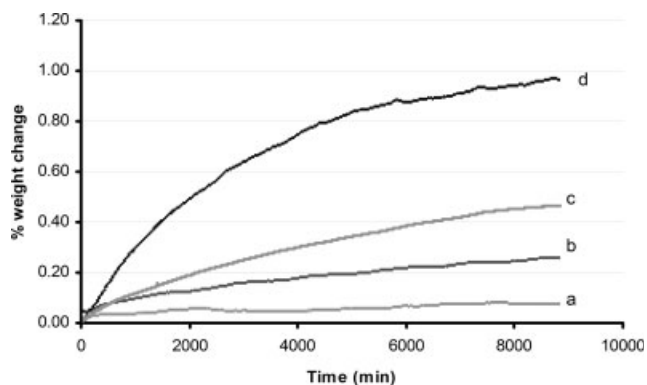
Figure 3 Sorption curves for benzaldehyde vapor in PP at vapor activity of 0.3 at 25°C. From bottom to top: (a) resin pellets, (b) sheet, (c) thermoformed sheet, and (d) atactic PP.

benzaldehyde by the sliced pellet indicate that a change in the characteristics of the surface or morphology of the surface (sliced versus whole resin pellets) significantly influences the sorption process. In the case of the whole pellet the surface is relatively homogeneous, but in the case of the sliced pellet the internal portion of the pellet became a part of the surface, thus the overall exposed area was a combination of surfaces with different characteristics. Also at equilibrium the sorption of benzaldehyde by the atactic PP was very high at 1.90% and this could be attributed to the 0% crystallinity of the polymer. It is well accepted that sorption and diffusion take place exclusively in the amorphous regions of polymers and that the crystalline zones are impermeable to permeant.[2,3] The results of this test confirmed that PP surface and bulk morphology had a major impact on the sorption of an organic vapor such as benzaldehyde due to the redistribution of free volume and crystalline regions.

### Sorption of benzaldehyde by different PP forms

The sorption levels of benzaldehyde in PP resin, extruded sheet, thermoformed container, and atactic PP when exposed to benzaldehyde at 0.3 VA and 25°C varied considerable (Fig. 3). The thermoformed sheet gained more weight (0.489%) than the extruded sheet (0.271%) and resin (0.077%) confirming the effect of processing on sorption.

Heat treatment of PP during the conversion process enhanced the molecular chain mobility and modified its original morphology. By cooling the article rapidly, the polymer chains were quenched, thereby causing the buildup of residual stresses in the polymer matrix. Once benzaldehyde interacted with the polymer, some of the stresses could be relieved, along with changes in the polymer morphology. This interaction did not alter the overall

crystallinity as reported by Qin et al.,[17] but affected the crystal size, distance between the lamellas, overall size, and the free volume (Fig. 3). Also, the much higher benzaldehyde sorption capacity for the amorphous atatic PP (0.989%), as compared to the semicrystalline homopolymer (Fig. 3), confirmed that free volume and crystallinity were important contributors for benzaldehyde sorption in semicrystalline PP.

Impact of benzaldehyde vapor activity on sorption behavior

The sorption trends for various PP forms at lower vapor activities are different from those observed at higher vapor activities (Fig. 4). As expected, the sorption capacity increased as the higher vapor activity increased and overall, the sorption curves flattened toward a maximum at the x-axis as it reached steady state. It is noteworthy that the sorption curve for the thermoformed sheet tended to achieve steady state much faster at high VA furthermore; the sorption curve of the pellets, sheet and thermoformed sheet were different at VA of 0.5 and at 0.9 which was not expected. This change in behavior may be
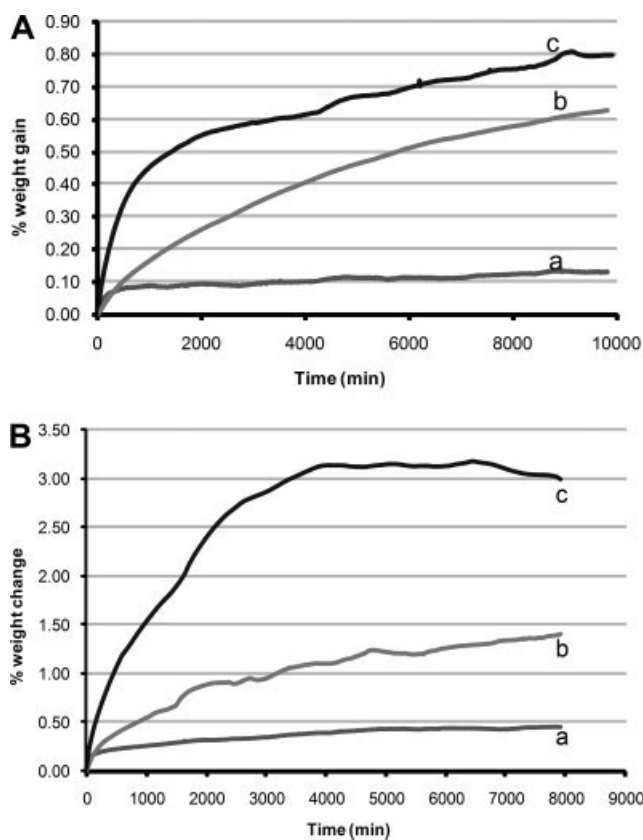
Figure 4 Sorption curves for benzaldehyde vapor in PP at 25°C at vapor activities of 0.5 (top) and 0.9 (bottom). From bottom to top: (a) resin pellets, (b) sheet, and (c) thermoformed sheet
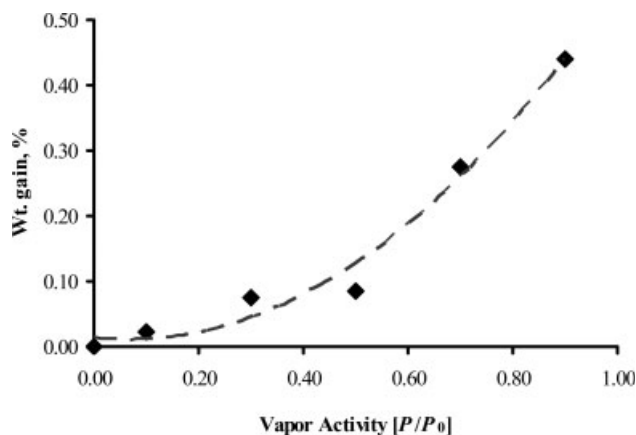
Figure 5 Sorption isotherm for benzaldehyde vapor in PP resin at 25°C. The prediction lines was calculated using the Flury–Huggins model.[18]

attributed to the different conversion process conditions used for the thermoformed container, extruded sheet, and pellets. The curve shape changes for the container and sheet at higher at the higher vapor activity of 0.9 versus at the lower vapor activity of 0.5. The thermoformed and extruded sheets were formed by quenching, therefore their free volume may be higher. And this may explain why they saturated faster with benzaldehyde at higher vapor activities. It is also possible that the distribution of the crystalline structure changes throughout the matrix, limiting further the free volume and allowing saturation to occur. The permeant also may be acting as a plasticizer at a vapor activity of 0.5, thereby increasing free volume. However at a vapor activity the benzaldehyde will saturate the free volume and behave as filler reaching steady state faster as shown by the thermoformed container at 0.9 vapor activity.

Benzaldehyde sorption isotherm

The shape of specific isotherms was determined by the polymer-penetrant interaction parameter and the crystallinity of the system. The sorption isotherm for benzaldehyde-rubbery PP resin pellets at 25°C was determined (Fig. 5) and the shape of this isotherm is typical for the sorption of organic vapors in rubbery polymers.

The shape of this isotherm is typical for the sorption of organic vapors in rubbery polymers. Thus, the Flory-Huggins eq. (1) was used to describe the sorption behavior:[18]

$$\ln(P/P_0) = \ln(V_1) + (1 - V_1) + \chi(1 - V_1)^2 \quad (1)$$

χ is the interaction parameter, V_1 is penetrant volume fraction, and P and P_0 are actual and saturated vapor pressures at specific temperatures, respec-

tively. The percent weight gain (%Wt. Gain) is related to the volume fractions of solvent and polymer, V_1 and V_2, respectively, by

$$\%\text{Wt. Gain} = 100 \cdot \frac{V_1 d_1}{V_2 d_2} \quad (2)$$

d_1 and d_2 are the solvent and polymer densities, respectively.

The Flory–Huggins interaction parameter χ has been used for many years to describe polymer solution behavior, with the χ_{12} parameter derived from the "New Flory Theory" being the most widely accepted for general use instead of the older χ. Patterson and coworkers have shown that χ_{12} can be calculated:[19]

$$\chi_{12} = \frac{V A_{12}}{RT} \quad (3)$$

V is the molecular volume of solvent; R is the gas constant (m^3 Pa)/(mol K); T is temperature in Kelvin, and A_{12} is calculated:[20]

$$A_{12} = [(\delta_{D2} - \delta_{D1})^2 + 0.25(\delta_{P2} - \delta_{P1})^2 + 0.25(\delta_{H2} - \delta_{H1})^2] \quad (4)$$

δ_D, δ_P, and δ_H the Hansen Solubility Parameters represent the contributions from the dispersion interaction, polar interaction, and hydrogen bonding, respectively; and the subscript 1 and 2 are for solvent and polymer, respectively.

CONCLUSIONS

The sorption of benzaldehyde in different forms of PP (resin, sheet, thermoformed sheet, and atactic PP) was studied at 25°C using a continuous gravimetric method. Each PP sample was placed in the gravimetric instrument and exposed to benzaldehyde of specific vapor activity for 6–7 days to follow the kinetics of benzaldehyde sorption for the PP sample. The sorption behaviors for these different forms of PP varied considerably depending on their thermal history, which has an impact on the morphology of the polymer matrix and free volume.

It was found that the characteristics of the surface area, polymer bulk properties, geometry, and morphology contributed to the sorption properties of PP. In a previous study it was reported that there were no changes in the overall percent crystallinity after extrusion and thermoforming,[17] indicating that most of the changes observed in this study may be due to changes in the free volume and the type of crystallite present in the polymer after the thermal processing. The interaction of PP with benzaldehyde further

modified the polymer morphology. The morphological changes might take place either on the surface or in the bulk of the PP. The container sorbed a greater amount of benzaldehyde than the extruded sheet and thermoformed container. Furthermore the sorption was higher at higher vapor activities future work should focus on correlating processing condition with specific morphological changes, either on the surface or in the bulk polymers, which will provide insight on how each phase affects the overall mass transfer behaviors.

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